HCM Newsletter

Ψ_k Network

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

Number 5 October 1994

Proposal: ERB4050PL930589
Contract: ERBCHRXCT930369

Coordinator: Walter Temmerman
E-mail: psik-coord@daresbury.ac.uk

Editorial

In the current Newsletter, apart from the abstracts and reports on workshops and some collaborative visits, we include an information on the topics of the next **European Research Conference** which will take place in The Netherlands next September, first announcement of the *ESF and HCM ψ_k-Network Workshop* on **Spin-orbit influenced spectroscopies of magnetic solids** organised by H. Ebert and G. Schütz, first announcement and application form of the Network Workshop on **Parallel Algorithms for Large Systems** organised within the Working Group H.e by the Messina Group in Taormina, two job announcements, and a comment by C. Molteni and V. Heine on **"How do Hartree-Fock and DFT-LDA compare?"**.

In the past month we made a lot of progress in including a detailed information about the Network, together with all the newsletters and the up-to date list of subscribers, into the **World Wide Web** (WWW). A trial service is already operational and can be accessed on: *http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html*
Incorporated in this is also an *anonymous ftp* which allows one to obtain the latex and poscript versions of all the past newsletters. If you have no access to WWW you can still ftp these newsletters using the *anonymous ftp* to: *ftp.dl.ac.uk* and then changing to the directory *HCM.newsletters*. Of course, we shall keep on emailing the future newsletters so that those who either have no access to WWW or prefer to deal with email can obtain all the information distributed within the Network. We shall inform you in the future newsletters when the process of transferring all the Network information to WWW has been completed.

We are very happy to receive all your abstracts which no doubt will be of importance for the renewal of the Network. However, we would like to stress a great need for acknowledging the HCM Network in all your publications that have resulted from genuine collaborations within the Network. This is going to be of paramount importance for Brussels. We would like to encourage you to many more collaborations within the Network, using its financial resources, and resulting in many scientific publications.

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

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

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

News from the Working Groups

Report on the Workshop of the Working Group H.c: Improved Density Functionals. Aarhus, June 9.-10. 1994

The workshop was attended by 44 people from 12 nations. 20 were network members. The program covered a wide range of approaches to the solid state electronic structure problem beyond the Local Density Approximation. Debates were lively. Correlated systems - transition metal oxides and f-electron metals - took up a large fraction of the workshop. Perhaps the best conclusion to be drawn is that while we have gained considerable insight into the physics of these systems the ultimate solution has not yet been found. Luckily. Then we continue to work.

It is my personal view that the primary goal of this workshop - to gather researchers and exchange knowledge about the performance of various attacks on the electronic structure problem - was well met.

Budget:
Travel covered by HCM (network members and invited speakers): 9.7 kECU; Local costs covered by HCM: 3.3 kECU; Total 13.0 kECU.

Program:

A. Zupan, Ljubljana,	*Hartree Fock*
F. Aryasetiawan, Lund,	*GW: Ni and NiO*
F. Manghi, Modena,	*3-body Scattering Theory*
E. K. U. Gross, Würzburg,	*Time-dependant DFT*
M. Foulkes, London,	*Quantum Monte Carlo*
R. Godby, Cambridge,	*Exact functionals for models*
P. Ziesche, Dresden,	*Modified HKS Scheme*
K.-H. Schwarz, Wien,	*Gradient Corrections*
P. Söderlind, Uppsala,	*Gradient Corrections*
M. Posternak, Lausanne,	*Model GW approach to TMO's.*
J. Zaanen, Leiden,	*Mean Field Theories and DFT*
V. Anisimov, Ekatarinenburg,	*LDA+U*
W. Temmerman, Daresbury,	*Self-Interaction Corrections*
L. Severin, Darmstadt,	*Orbital Polarisation Schemes*
L. Sandratskii, Darmstadt,	*Non-Collinear Magnetism*
J. Furthmüller, Wien	*GGA and phases of As, Sb, Se and Te*

Attendants:
A. Zupan, Ljubljana. **F. Aryasetiawan**, Lund. **E. K. U. Gross**, Würzburg. **M. Foulkes**, London. **R. Godby**, Cambridge. **K.-H. Schwarz**, Wien. **P. Soderlind**, Uppsala. **J. Zaanen**, Leiden. **V. Anisimov**, Ekatarinenburg. **W. Temmerman**, Daresbury. **L. Severin**, Darmstadt. **F. Manghi**, Modena. **P. Ziesche**, Dresden. **R. Magri**, Modena. **C. Arcangeli**, Konstanz. **Z. Szotek**, Daresbury. **U. Schönberger**, Stuttgart. **C. Kruse**, Stuttgart. **N. Harrison**, Daresbury. **M. Posternak**, Lausanne. **R. Monnier**, Zurich. **P. Kratzer**, Lyngby. **M. Battocletti**, Munchen. **J. Fürthmueller**, Wien. **L. Sandratskii**, Darmstadt. **H. G. Bekker**, Entschede. **M. Lüders**, Würzburg. **T. Korhonen**, Espoo. **M. Nekovee**, Nijmegen. **A. Jeziersky**, Poznan. **I. Gorzcyga**, Warschawa. **U. von Barth**, Lund. **M. Hindgren**, Lund. **T. Holleboom**, Lund. **B. Holm**, Lund. **M. Springer**, Lund. **P.-S. Svendsen**, Lund. **J. Forstreuter**, Dresden. **M. Fuchs**, Berlin. **A. Svane**, Århus. **N. E. Christensen**, Århus. **W. Schulz**, Århus. **J. Lægsgaard**, Århus. **J. Rotvig**, Copenhagen.

(A. Svane)

Report by G. Y. Guo on a collaborative visit to IFF, Forschungszentrums Juelich on 25-26 April 1994

Last April, I spent nearly a month in Muenchen, working with H. Ebert on a multiple scattering theory of magnetic dichroism in angle resolved core level photoemission experiments, and also on the spin-polarized, relativistic band theory of the magneto-optical Kerr effect. This collaborative visit was funded by the European Science Foundation (ESF) through a grant from its Relativistic Effects in Heavy Elements network. During my stay in Muenchen, I made a brief trip to Juelich using some fund from the Psi-K network (2nd class rail tickets and one night accommodation). I had extensive and stimulating discussions with S. Bluegel on magnetic overlayers, with P. Dederichs on magnetic multilayers, and Eberhardt and his experimental colleagues on magnetic x-ray dichroism.

(G.Y. Guo)

Report on a scientific collaboration within Ψ_k Network

B.Ginatempo (Messina), J.B. Staunton (Warwick)
Warwick, July 9th-20th, 1994

The visit began with a discussion of the role of Electronic Topological Transitions of Fermi Surfaces on several physical properties of binary solids solutions. We then went on to adapt a code which calculates the electronic structure of disordered systems via the Bloch Spectral Function so that it can deal with effective one electron potentials of ASA type in addition to muffin-tin potentials.

Calculations of the Fermi energy electronic structure of a compositionally disordered $Fe_{0.80}$-$Al_{0.20}$ alloy, both in its paramagnetic (Disordered Local Moment model, DLM) and ferromagnetic phases were carried out and we obtained the following results:
i) The Bloch Spectral Function at the Fermi energy is rather featureless for the paramagnetic alloy. In other words the strong compositional and spin disorder makes the Fermi surface practically undetectable.
ii) The Bloch Spectral Function at the Fermi energy of the ferromagnetic alloy is sharp for the majority spin but featureless and mostly broadened for the minority spin. As a consequence, a very well defined Fermi surface does exist for the majority spin. This Fermi surface consists of one sheet around the Γ point broken by a neck around the N point, and shows a nicely flat sheet perpendicular to the direction Γ-P, where it has a flexus. We connected these results to calculations, which had been carried out prior to the visit, of the compositional correlation functions of the alloy in both its ferro- and paramagnetic phases.

Our conclusion is that "spin ordering" allows the existence of a sharp Fermi surface. As a consequence, the rearrangement of charge which occurs as the ferromagnetic alloy begins to order is less efficiently screened by the majority spin electrons, and this causes the system to become unstable to compositional fluctuations along the direction Γ-P (1/2,1/2,1/2). This is, in our opinion, the reason why, on cooling from high temperatures in the paramagnetic phase, the system shows strong DO_3-type correlations (concentration wavevector (1,0,0)), whereas at lower temperatures in the ferromagnetic phase the system manifests B_{32}-type correlations (wavevector (1/2,1/2,1/2)). These features are seen in the neutron scattering data of Schweika et al., and are also substantiated by our 'first principles' compositional correlation function calculations.

(B.Ginatempo)

Report by M.W. Finnis on his collaborative visits to U.K. in August 1994

As in my proposal, I visited the TCM Group in the Cavendish Laboratory, Cambridge, for three weeks and the Materials Department in Oxford for a week. During the first period I also spent a day at the University of Keele (Mike Gillan).

In Cambridge my first task was to write a "Comment" together with Richard Needs, on a recent Phys. Rev. Lett. by Smith et al, which criticises our surface energy calculations. We maintain that their criticism is invalid, and I hope the comment and any reply will be published this year. I also discussed with Richard Needs the problem of calculating image potentials, in connection with a paper by myself and coworkers on this subject which I will shortly submit.

With Volker Heine and others I discussed calculations of Ga in Al, in particular how to calculate grain boundary segregation and its effect on interfacial energy. We also discussed the interpretation of calculations of the deformation of Al. On a different topic, the calculation of point defect energies in binary ordered alloys, I was helped by discussions with Chris Nex. I have set up a scheme by which the concentrations of point defects as a function of temperature may be obtained from the basic defect energies which are calculated in ab initio or empirical models.

In Keele we discussed further collaboration on oxide-metal interfaces. Having completed Nb/sapphire calculations, we plan to apply CASTEP to Al/spinel, Ag/spinel and Nb/TiO2. The Keele group are getting useful experience with the modelling of metal oxides and with technical improvements in CASTEP, which we would benefit from in Stuttgart.

In Oxford I worked with Tony Paxton on LMTO calculations of Nb/Al2O3 and pure Al2O3. We are assessing the usefulness of the LMTO approach for these rather loosely packed systems. Our further plan is to look at densities of states and core level shifts in order to provide a more accurate theoretical framework for interpreting the near-edge structure in HREELS, which is being investigated in an experimental group in Stuttgart.

I have proposed to divide the cost between the Large Systems and the Oxides Working Groups.

(M.W. Finnis)

Report on the collaborative visit of B. Kohler (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin) to K. Schwarz and P. Blaha (Technical University Vienna) September 5-9, 1994

The main purpose of this visit was to implement the direct evaluation of atomic forces into the "official version" of the linear augmented plane-wave (LAPW) code WIEN developed by P. Blaha, K. Schwarz, *et al.*. During the stay we extended the force formalism employed [R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).] in order to make it applicable to local orbitals too. The evaluated atomic forces are highly accurate and can be used for an efficient structure optimization of poly-atomic systems [B. Kohler, S. Wilke, and M. Scheffler, to be published in Comp. Phys. Commun.].
Further aspects discussed were:

- A recently developed program to create LAPW start densities
- Inclusion of local orbitals in the LAPW basis set
- Improvements in the UNIX environment to enable a more efficient handling of the WIEN package
- Efficient methods to optimize structures (e.g. molecular dynamics simulations, variable metric methods, ...)
- Program tools to set up and test symmetry operations
- An WIEN extension to enable pseudo-potential calculation

Many of these enhancements will be part of the new version WIEN95.

(Bernd Kohler)

European Research Conferences: Electronic Structure of Solids

The next conference in this series will focus on

ITINERANT MAGNETISM

Lunteren, The Netherlands, 9-14 September 1995

Conference Chairman: Professor B.L. Gyorffy (Bristol),

Assistant Chairman: Dr. S. Blügel (Jülich)

Topics selected for special emphasis:

- Spin-Polarised Band Theory (orbital magnetism, heavy fermions, spin fluctuations, ...)
- Magnetism at Surfaces and Interfaces (perpendicular surface magnetism, exchange anisotropy, ...)
- Magnetic Metallic Multilayers (oscillatory coupling, giant magnetio-resistance, ...)
- Magnetism in Disordered Systems (spin glasses, magnetic alloys, metallic glasses, ...)
- 'LDA+Hubbard U' (simple effective Hamiltonians from LDA calculations for HTC, heavy fermions, ...)

Suggestions for speakers or topics are still welcomed and can be submitted to Professor B.L. Gyorffy (blg@siva.bristol.ac.uk).

FIRST ANNOUNCEMENT

ESF and HCM ψ_k-Network Workshop

Spin-orbit influenced spectroscopies of magnetic solids

Herrsching (Germany), 20-23 April, 1995

Organisers: H. Ebert and G. Schütz

The aim of the workshop is to bring together researchers from all of Europe active in the field of "Spin-orbit influenced spectroscopies of magnetic solids" and related topics to present and discuss their latest results and ideas. There will be around 18 invited contributions dealing with spin-polarisation of photo-electrons from para- and ferromagnets, core level spectroscopies, linear and circular magnetic dichroism, magneto-optical Kerr-effect as well as other closely related phenomena.

For details please contact:

Prof. Dr. H. Ebert
Inst. für Physik. Chemie,
Universität München,
Theresienstr. 37-41,
D-80333 München
Tel.: (089) 23 94 - 46 42 / - 42 18
Fax.: (089) 28 05 - 248 and 23 94 - 46 42
Email: he@gaia.phys.chemie.uni-muenchen.de

Prof. Dr. G. Schütz
LS für Exp.physik II,
Universität Augsburg,
Memmingerstr. 6,
D-86135 Augsburg
Tel.: (0821) 59 77 - 3 15
Fax.: (0821) 59 77
Email: schuetz@phibm30c.physik.uni-augsburg.de

HCM Ψ_k Network Workshop

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

INTERNATIONAL WORKSHOP

on Parallel Algorithms for Large Systems

Taormina, 26-28th November 1994

1st Circular

Workshop also sponsored by Presidenza delle Regione Siciliana and Comune di Taormina

GENERAL INFORMATIONS

Purpose: To discuss and exchange expertise and ideas about the chances and the challenges offered by parallel computing to the condensed matter physicists.

Arrival: November 25th, evening
Departure: November 28th, lunchtime

Location: The workshop will be held in Taormina (Sicily), at the Jolly Diodoro Hotel. Workshop special rates are:
Half board in double room 80,000 Italian Liras
Full board in double room 100,000 Italian Liras
Single room supplement 30,000 Italian Liras

Finance: Ψ_k Network Board will cover networkers and invited speakers travel expenses and subsistence (40 ECU/day rate). HCM rate is not sufficient (at today ECU/lira exchange rate) to cover the half board (double room occupancy) cost, but the local organization has been sponsored by Regione Siciliana Presidence, in order to cover the prize difference, for each networker and to take care of the organization expenses.

Limitations: We regret that, due to budget reasons, we must keep within the following limits:
no. of local grants for networkers 60

no. of contributed talks 30

Talk facilities: An overhead and a slide projectors will be provided. Speakers having special requests should specify those in the Application Form.

Guests: Participants guests are welcomed. They will be charged for their stay at the above reduced rates.

How to reach Taormina:
plane: Fly to Catania Airport (there are charter flights from most european countries)
train: Travel to Taormina railway station
Further details after sending the Application Form

If you are interseted please fill in the application form attached below and send exclusively by **fax** to the address:

Mediterranea Meetings
FAX +39-90-2925794
Via U. Bassi 136T
98123 Messina
Italy
Phone: +39-90-692854

DEADLINE OCTOBER 28th

Please send the abstract, in latex or postscript (HCM newsletter style), to
e-mail: bg@vulcano.unime.it

Contact for any problem or informations:
B. Ginatempo or E. Bruno
Dipartimento di Fisica
Salita Sperone 31
98166 Messina
Italy
Phone +39-90-393713 or 6763233
FAX +39-90-6765041
e-mail: bg@vulcano.unime.it

HCM WORKSHOP

on Parallel Algorithms for Large Systems

Taormina, 26-28th November 1994

APPLICATION FORM

NAME: .....**FIRST NAME**:.....
INSTITUTION: .....
.....
.....
POSTAL ADDRESS: .....
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PHONE: .....**FAX**: .....
e-mail: .....

ARRIVAL DATE: .....**DEPARTURE DATE**: .....

Please leave blank where inappropriate

I would like to present a contributed talk entitled(abstract on a separate sheet):
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I will come with no......**guests**

I would like a single room: **YES** **NO**
I would like to share the room with: .....

I require a vegetarian menu: **YES** **NO**

Other special requests:.....
.....

ANNOUNCEMENT

POST-DOCTORAL FELLOWSHIP FOR FIRST PRINCIPLES CALCULATIONS OF MAGNETIC ANISOTROPIC EFFECTS IN ALLOYS.

A post-doctoral research position funded by the Engineering and Physical Sciences Research Council (U.K.) will become available after 1 January 1995 at the University of Warwick. It will be associated with a project on the theoretical study of magnetocrystalline anisotropy and atomic short range order in alloys. The work to be carried out in collaboration with J.B.Staunton will involve building upon the SCF-KKR-CPA theory of alloys and fully relativistic, spin-polarised scattering theory in order to investigate magnetic anisotropic effects in alloys.

Further details may be obtained by e-mail from phrjz@weedy.warwick.ac.uk. Applications by post, including the names of two referees, should be made to J.B.Staunton, Department of Physics, University of Warwick, Coventry CV4 7AL, U.K. or by e-mail to the address above.

ANNOUNCEMENT

POST-DOCTORAL POSITION

The U.K. Car-Parrinello Consortium

First-Principles Simulation of Materials on High-Performance Computers

A two-year post-doctoral position is available immediately to work with the U.K. Car-Parrinello consortium (UKCP) developing code for first-principles simulation on the Cray T3D machine recently installed in Edinburgh, and subsequent high-performance computers.

UKCP is a consortium of computational condensed-matter groups based at Bath (Bird), Cambridge (Payne, Heine, Bristowe), Daresbury (Durham), Edinburgh (Ackland), Keele (Gillan) and Oxford (Sutton, Madden). The aim of the consortium is to develop techniques and codes for the first-principles simulation of materials on parallel computers, and the use of these codes to tackle 'grand-challenge' scientific problems. The consortium has been in existence for four years and has built up extensive expertise in parallel first-principles simulation through collaborative projects done on the 64-node Meiko Computing Surface at Edinburgh University, and a similar Intel machine at Daresbury Laboratory. The methods used by the consortium are based on density-functional theory and pseudopotentials, and exploit the Car-Parrinello principle of global minimisation with respect to occupied electronic orbitals.

In the Summer of 1994, a 256-processor Cray T3D was installed at Edinburgh Unviersity. The new machine has a theoretical peak performance of 38 Gflops and a total of 16 Gbytes of memory. UKCP expects to be given a substantial allocation of time on the machine, which will be used for a range of exciting new scientific projects.

The present post-doctoral position has the aim of developing and optimising code to exploit the power of the new machine for first-principles simulation. It is planned that there will be a strong focus on order-N techniques for simulating very large systems.

Because of the emphasis on code-development, candidates for the position will need to demonstrate outstanding ability and substantial experience in writing code for supercomputers, and preference will be given to those having expertise in parallel computing. Research experience in computational condensed-matter physics, chemistry or materials science is also needed for the position, and a good knowledge of electronic-structure theory is highly desirable.

It is envisaged that the research position will be based in the Cavendish Laboratory, Cambridge University, though there may be some flexibility in this. The salary is on the normal U.K. Research Council scale, and will depend on age and experience.

Potential candidates should enquire in the first instance to Professor M. J. Gillan, who will provide more detailed information. This can be done by replying to the present mail (address: pha71@keele.ac.uk), by telephoning ((+44)-782- 583326), by sending a fax ((+44)-782-711093) or by writing to : Physics Dept., Keele University, Keele, Staffs. ST5 5BG, U.K.

Comment on

HOW DO HARTREE–FOCK AND DFT–LDA (DENSITY FUNCTIONAL THEORY IN LOCAL DENSITY APPROXIMATION FOR EXCHANGE AND CORRELATION) COMPARE?

A year or so ago it became apparent that some results of Hartree–Fock (HF)[1] and DFT–LDA[2] calculations, both on GaAs, differed in important regards by a factor of about three. The issue was the difference between the equilibrium energies of the stable tetrahedral ZnS structure and the denser metastable NaCl one, as well as the transition pressure between them. The energy minima came at very much the same volumes in the two calculations, but the energy scales simply differed by a factor of about three.

Since then, the matter has been investigated and cleared up with interesting conclusions. Incidentally the DFT–LDA total energy calculations, which were quite old, were repeated and confirmed with small deviations[3].

Various approximations to add the correlation energy to the HF calculations have been tested[4]. They include: plain Hartree–Fock (HF); Hartree–Fock with an added correlation correction obtained by integrating the Perdew functional of the HF self–consistent electron density (HF+C); Hartree–Fock with a LDA correction (Dirac functional for the exchange and Ceperley–Alder functional as parametrized by Perdew and Zunger for correlation) with the self–consistent HF electron density (HF–LDA). The corresponding results concerning the equilibrium energy difference between the ZnS and the NaCl geometries are summarized in the following table, together with the DFT–LDA datum.

	HF	HF+C	HF–LDA	DFT–LDA
$E^{eq}_{NaCl} - E^{eq}_{ZnS}(eV/cell)$	2.26	1.67	0.81	0.67

To cut a long story short, there are two main conclusions. Firstly the experimental transition pressure agrees more or less with the DFT–LDA result. Secondly the HF calculations also agree with the DFT–LDA results if one adds the correlation energy using the LDA approximation applied as a retrofit to the electron density obtained from HF. We may thus conclude that it is the approximation used to deal with correlation that deeply affects quantities as the equilibrium energy differences between different crystalline phases.

The DFT–LDA and HF+C results for the ZnS and NaCl structures of GaAs have been used as distinct input data sets to fit two suitable Tight–Binding (TB) potentials for Molecular Dynamics simulations. The corresponding total energy curves, together with a comparison between the MD results for liquid GaAs obtained with the two TB parametrizations may be found in Ref.5.

C.Molteni and V.Heine
Cavendish Laboratory, Cambridge (UK)

[1] C.Molteni, L.Miglio, L.Colombo and M.Causà, Il Vuoto **4**, 94 (1992)
[2] S.Froyen and M.Cohen, Phys.Rev. **B 43**, 447 (1982)
[3] S.de Gironcoli, private communication (1993)
[4] M.Causà, private communication (1993); M.Causà and A.Zupan, Chem.Phys.Lett. **220**, 145 (1994); M.Causà and A.Zupan, Int.Journ.Quant.Chem., in press (1994)
[5] C.Molteni, L.Colombo and L.Miglio, J.Phys.:Condens.Matter **6**, 5243 (1994); C.Molteni, L.Colombo and L.Miglio, J.Phys.:Condens.Matter **6**, 5255 (1994)

Magnetic anisotropy of a free-standing Co monolayer and of multilayers which contain Co monolayers

G.H.O. Daalderop, P.J. Kelly and M.F.H. Schuurmans
Philips Research Laboratories, Prof. Holstlaan 4,
5656 AA Eindhoven, The Netherlands

Abstract

The magnetocrystalline anisotropy energy of a free-standing [111] Co monolayer has been calculated from first principles by means of the linear muffin-tin orbital method in the atomic-spheres approximation. The results are used to analyse those obtained previously for [111] Co_1/Pd_2 and Co_1/Ag_2 multilayers. Although the magnetization of both multilayers is predicted to be oriented perpendicular to the plane of the multilayers, the easy axis of the Co monolayer is predicted to lie in-plane. These results can be understood in terms of the energy bands at the high-symmetry points of the Brillouin zone only. Co_1/Pd_2 is found to have a perpendicular anisotropy because the Fermi energy is located much closer to states which have mainly Co $d_{x^2-y^2}$ and d_{xy} character than it does in the free-standing monolayer. These states are degenerate in the absence of spin-orbit coupling as a consequence of the threefold symmetry. The anisotropy energy is enhanced by the hybridization of the Pd d and Co d states and the large value of the Pd d spin-orbit coupling parameter. The smaller perpendicular magnetic anisotropy of a Co_1/Ag_2 multilayer can be attributed to the increased band-filling of the Co d bandstructure, as well as to a smaller hybridization between Ag and Co d states.

(accepted for publication in Physical Review B)
Manuscript available from kelly@prl.philips.nl

Theory of Acetylene Adsorption on Cu(111): A New Surface Binding Mechanism

K. Hermann[1] and M. Wittko[2]

[1] Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

[2] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek, 30239 Cracow, Poland

Abstract

Recent photoelectron diffraction (PED) data suggest that the adsorption of C_2H_2 on Cu(111) is combined with large structural changes of the adsorbate while the overall adsorbate-substrate binding seems weak. Cluster model calculations based on ab initio Hartree-Fock and correlated wavefunctions for $Cu_7C_2H_2$ and preliminary results for $Cu_{22}C_2H_2$ show details of the C_2H_2/Cu(111) chemisorption bond which can explain the geometric rearrangement of the adsorbate. In the calculations the optimized C-C distance of adsorbed C_2H_2 is found to be greatly increased with respect to that of the free molecule. Thus, C_2H_2 can stabilize with its C-C axis parallel to the Cu(111) surface over a bridge site where the two centers occupy 3-fold hollow sites. This is in agreement with recent experimental PED results. Further, the C-H axes are tilted with respect to the C-C axis pointing away from the surface. As a result, the overall weak C_2H_2-Cu(111) binding is determined by a competition between energy cost due to geometry changes in the adsorbate molecule and energy gain due to C-Cu bond formation of the distorted molecule. Here correlation contributions to binding are found to be necessary for a correct evaluation of the energetics. The present type of surface bond formation where structural changes become important may be more general and applicable to other organic adsorbate systems.

(submitted to Surface Science)

Manuscripts can be obtained from: `hermann@fhi-berlin.mpg.de`

The Projector Augmented Wave Method

P.E. Blöchl
IBM Research Division; Zurich Research Laboratory;
CH-8803 Rüschlikon; Switzerland

Abstract

An approach for electronic structure calculations is described that generalizes both the pseudopotential method and the linear augmented plane-wave (LAPW) method in a natural way. The method allows high-quality first-principles molecular dynamics calculations to be performed using the original fictitious Lagrangian approach of Car and Parrinello. Like the LAPW method it can be used to treat first-row and transition-metal elements with affordable effort and provides access to the full wave function. The augmentation procedure is generalized in that partial-wave expansions are not determined by value and derivative of the envelope function at some muffin-tin radius but rather by the overlap with localized projector functions. The pseudopotential approach based on generalized separable pseudopotentials can be regained by a simple approximation.

(submitted to Phys. Rev. B on 13. June 1994)

Finite-Temperature Characterization of Ferrocene from First-Principles Molecular Dynamics Simulations

Peter Margl, Karlheinz Schwarz
Technical University of Vienna,Getreidemarkt 9/158,
A-1060 Vienna, Austria
Peter E. Blöchl
IBM Research Division, Zurich Research Laboratory,
CH-8803 Rüschlikon, Switzerland

Abstract

A first-principles molecular dynamics calculation of ferrocene ($Fe(C_5H_5)_2$) at 300 K, based on the local density approximation, is presented. Kohn-Sham equations and forces on the atoms are obtained using the projector augmented wave technique. Frequencies and eigenmodes are derived by fitting a system of harmonic oscillators to the molecular dynamics trajectory. Frequency shifts for deuterated ferrocene ($Fe(C_5D_5)_2$,ferrocene-d_{10}) and the corresponding eigenvectors are obtained by diagonalizing the dynamical matrix after renormalizing it according to the changed masses. Most experimental and theoretical frequencies agree to about 2.5% (or 20 wave numbers), with the exception of six modes for which a new assignment is proposed.

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Reprints are availablefrom blo@zurich.ibm.com

Fluxional Dynamics of Beryllocene

Peter Margl, Karlheinz Schwarz
Technical University of Vienna,Getreidemarkt 9/158,
A-1060 Vienna, Austria
Peter E. Blöchl
IBM Research Division, Zurich Research Laboratory,
8803 Rüschlikon, Switzerland

Abstract

Structure and dynamical properties of beryllocene ($Be(C_5H_5)_2$) at finite temperature have been investigated using the first-principles molecular dynamics method of Car and Parrinello in combination with the projector augmented wave (PAW) method and the gradient-corrected local density approximation (GC-LDA). The GC-LDA ground state of $Be(Cp)_2$ is the so-called "slipped-sandwich" structure with one η^5- and one η^1-coordinated ring. All other conformations investigated were higher in energy by 5-10 kJ·mol^{-1}. We find two mechanisms for intramolecular rearrangements, having activation barriers of 5 and 8 kJ·mol^{-1}, resp. The rate of hapticity change in vacuum at 400 K is of the order of $1–4\times10^{12}$ s^{-1}.

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Preprints available from blo@zurich.ibm.com

Theoretical investigation of orientation dependence of magneto-optical Kerr effect in Co

G. Y. Guo[a] and H. Ebert[b]
[a]DRAL, Daresbury Laboratory, Warrington WA4 4AD, UK
[b]Institute for Physical Chemistry, University of Muenchen,
Theresienstr. 37, D-80333 Muenchen, FRG

Abstract

The first-principles spin-polarized, relativistic linear muffin-tin orbital (SPRLMTO) method has been applied to calculate electronic and magneto-optical properties of Co in both fcc and hcp structures. In particular, the magneto-optical properties have been calculated for several magnetization directions in order to study their magnetization orientation dependences. A pronounced anisotropy in the polar Kerr effect is found for hcp Co whilst the magneto-optical properties of fcc Co are predicted to be insensitive to the magnetization direction. Moreover, this magneto-optical anisotropy in hcp Co is found to be correlated with the presence of a large anisotropy in the orbital magnetic moment and orbital hyperfine field. Changing the structure from fcc to hcp gives rise to even greater changes in the magneto-optical properties of Co. Calculated Kerr angles and ellipticities are in reasonable agreement with the latest experiment.

(Phys. Rev. B (Rapid Comm.), 1994 (in press))
Postscript file can be obtained from: G.Y. Guo@dl.ac.uk

High-dimensional quantum dynamics of adsorption and desorption of H_2 at Cu(111)

Axel Gross, Bjørk Hammer[1] , Matthias Scheffler,
and Wilhelm Brenig[2]
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-14195 Berlin, Germany
[1] Present address: Physics Department, Technical University of Denmark,
DK-2800 Lyngby, Denmark
[2] Physik-Department T30, Technische Universität München,
D-85747 Garching, Germany

Abstract

We performed high-dimensional quantum dynamical calculations of the dissociative adsorption and associative desorption of H_2/Cu(111). The potential energy surface (PES) is obtained from density functional theory calculations. Two regimes of dynamics are found, at low energies sticking is determined by the minimum energy barrier, at high energies by the distribution of barrier heights. Experimental results are well-reproduced qualitatively, but some quantitative discrepancies are identified as well. Our results suggest that the spatial corrugation of the PES resembles that of reality.

(Submitted to Phys. Rev. Lett.)
REVTEX version can be obtained from: axel@theo22.RZ-Berlin.MPG.DE

Application of generalized gradient approximations: The diamond to β-tin phase-transition in Si and Ge

N. Moll, M. Bockstedte, M. Fuchs, E. Pehlke, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-14195 Berlin (Dahlem), Germany

Abstract

Generalized gradient approximations (GGA) for the exchange-correlation energy have been suggested to improve upon the local-density approximation (LDA) in density-functional theory. It has been demonstrated by various authors that the gradient correction suggested by Becke for the exchange functional and Perdew for the correlation energy, as well as the recent GGA by Perdew and Wang (1991) yield improved cohesive energies for solids, correcting for the overbinding in LDA. In this paper we focus on a structural phase transition of Si, which under pressure transforms from the diamond structure to the β-tin structure. The LDA fails in yielding an accurate value for the coexistence pressure: the theoretical prediction is 80 kbar, as opposed to 125 kbar found experimentally. In contrast, both gradient-corrected schemes yield a coexistence pressure much closer to experiment (146 kbar for the Becke-Perdew and 122 kbar for the Perdew-Wang exchange-correlation functional). Ge undergoes a similar transition at around 107 kbar. In this case already the LDA result for the coexistence pressure (94 kbar) is rather close to experiment, while the pressure is overestimated by the Becke-Perdew GGA (154 kbar). The Perdew-Wang GGA, on the other hand, yields a pressure of 115 kbar, which is even somewhat, but not significantly, closer to the experimental value than the LDA result.

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REVTEX version can be obtained from: moll@theo25.RZ-Berlin.MPG.DE

Hydrogen Adsorption on and Desorption from Si(001)

E. Pehlke and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,Faradayweg 4-6,
D-14195 Berlin (Dahlem), Germany

Abstract

Recent experiments have lead to apparently contradictory results for the adsorption barrier of hydrogen molecules adsorbing on, or desorbing from, a Si(001) surface: While the observed small sticking coefficient of hydrogen molecules indicates a substantial adsorption barrier, no such barrier is observed in desorption. To investigate the mechanism behind this puzzling result, we have carried out *ab initio* total-energy calculations to map the potential energy hypersurface of an H_2 molecule in front of a Si(001) surface. The impinging molecule experiences a large barrier, as the Si atoms cannot relax adiabatically. H atoms adsorbed on the surface, however, wait for an appropriate fluctuation of the Si positions and desorb, following a path close to the minimum energy path for the adiabatically relaxed surface. Thereby they only transverse a small barrier.

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LATEX version can be obtained from: pehlke@theo25.RZ-Berlin.MPG.DE

Linear Muffin Tin Orbital method with multiple orbitals per L channel

F. Aryasetiawan and O. Gunnarsson
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart
Federal Republic of Germany

Abstract

A method for calculating both the valence and high lying conduction bandstructure of a solid is developed. The basis functions are Linear Muffin-Tin Orbitals with multiple orbitals per angular momentum channel corresponding to different energies. In contrast to the conventional panelling method, our method treats the valence and conduction bands on equal footing so that the wavefunctions are orthogonal, which avoids the non-orthogonality problem when calculating transition matrix elements between occupied and unoccupied states and the discontinuity in the bandstructure. An empty lattice test reproduces the free-electron band up to at least 50 eV. The method is applied to Nickel and a comparison with a different approach based on a modified Linear Augmented Plane Wave method is made.

(published in Phys. Rev. B)
Latex-file available from: fa@TeorFys.lu.se

A Product Basis Method for Calculating Dielectric Matrices

F. Aryasetiawan and O. Gunnarsson
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart
Federal Republic of Germany

Abstract

We present a method for calculating dielectric matrices of periodic systems. Unlike the conventional method which uses a planewave basis, the present method employs a product basis, which in the Linear Muffin Tin Orbital formalism consists of products of orbitals. The method can be used for any system, *sp* as well as narrow band ones. We demonstrate the applicability of our method by calculating the energy loss spectra of Ni, including local field effects which require the full dielectric matrix. Good agreement with experiment is found. The small number of basis functions makes the method suitable for self-energy calculations within the GW approximation, without making the so called plasmon pole approximation for the dielectric matrix.

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Latex-file available from: fa@TeorFys.lu.se

Energy Loss Spectra and Plasmon Dispersions in Alkali Metals: Negative Plasmon Dispersion in Cs

F. Aryasetiawan

Max-Planck-Institut für Festkörperforschung

Heisenbergstrasse 1, 70569 Stuttgart, Federal Republic of Germany

K. Karlsson

Institute for Theoretical Physics, University of Lund,

Sölvegatan 14A, 22362 Lund, Sweden

Abstract

We present *ab initio* calculations of the energy loss spectra and plasmon dispersions of the alkali metals Na, K, Rb and Cs within the random phase approximation, including bandstructure effects and core electrons as well as local field effects, due to inhomogeneity in the induced charge density. Bandstructure effects are found to cause a negative dispersion in Cs.

(published in Phys. Rev. Lett.)

Latex-file available from: fa@TeorFys.lu.se

The electronic structure of NiO in the GW approximation

F. Aryasetiawan and O. Gunnarsson
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart, Federal Republic of Germany

Abstract

We present a method for calculating the self-energy in the GW approximation that can be applied to systems containing $3d$ and $4f$ electrons. The method is applied to NiO and a gap of $\sim$ 5.5 eV is obtained, which is in reasonable agreement with the experimental value of 4.0 eV. The local density O p-band is also improved. The high binding energy satellite at 8 eV, however, is not obtained and there is no substantial increased of O p-character at the top of the valence band compared to the local density result. Based on our results, we discuss to which extent the GW approximation is capable of describing highly correlated systems such as NiO.

(submitted to Phys. Rev. Lett.)
Latex-file available from: fa@TeorFys.lu.se

Jahn-Teller effect and on-site interaction for C_{60}^{n-}

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung,
D-70506 Stuttgart, Germany

Abstract

The lowering of the total energy due to the electron-vibration interaction is calculated for C_{60}^{n-} molecules and the electron-vibration contribution to the on-site interaction is obtained. It is found that C_{60}^{n-} is in the intermediate- to strong-coupling limit, and that the vibration contribution to the on-site interaction is of the order -0.1 to -0.2 eV for $n = 1$ and $n = 3$ and of the order +0.3 eV for $n = 2$ and $n = 4$.

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Latex-file available from: gunnar@radix3.mpi-stuttgart.mpg.de

Photoemission Spectra of C_{60}^-; Electron-phonon coupling, Jahn-Teller Effect and Superconductivity in the Fullerides

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung,
D-70506 Stuttgart, Germany
H. Handschuh, P.S. Bechthold, B. Kessler, G. Ganteför, and W. Eberhardt
Forschungszentrum Jülich GmbH,
Institut für Festkörperforschung,
D-52425 Jülich, Germany

Abstract

A high-resolution experimental photoemission spectrum of C_{60}^- is compared with calculations including the Jahn-Teller effect on the LUMO and multiple phonon satellites. The spectra show discrete loss features due to the excitation of phonons. From the intensity of these features, electron-phonon coupling constants are derived, which support the electron-phonon mechanism for superconductivity. The systematic deviations from previously calculated coupling constants are discussed in detail.

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Latex-file available from: gunnar@radix3.mpi-stuttgart.mpg.de

Corrections to Migdal's theorem for spectral functions. A cumulant treatment of the time-dependent Green's function

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung,
D-70506 Stuttgart, Germany
V. Meden and K. Schönhammer
Institut für Theoretische Physik,
Universität Göttingen,
D-37073 Göttingen, Germany

Abstract

The electron spectral function is calculated for a model including electron-phonon coupling to Einstein phonons. The spectrum is studied as a function of the electronic band width and the energy ε_k of the level from which the electron is removed. A cumulant expansion is used for the time-dependent Green's function, and the second and fourth order cumulants are studied. This approach is demonstrated to give accurate results for an exactly solvable two-level model with two electronic levels coupling to local phonons. For a one-band, infinite, three-dimensional model the cumulant expansion gives one satellite in the large band width limit. As the band width is reduced, the spectrum calculated with the fourth order cumulant develops multiple satellites, if ε_k is close to the Fermi energy E_F, and as the band width becomes small results similar to the two-level model are obtained. If ε_k is more than a phonon energy below E_F, the spectrum instead shows a very broad peak, due to the decay of the hole into a hole closer to E_F and a phonon. If the spin degeneracy of the electrons is taken into account, the broadening due to the deacy of a hole into a hole closer to E_F and an electron-hole pair becomes important, even if ε_k is closer to E_F than the phonon energy. The validity of Migdal's theorem for A_3C_{60} (A=K, Rb) is discussed. The inter sub band electron-phonon coupling is appreciable for A_3C_{60}, and it may be argued that the effective band width is large. It is shown that Migdal's theorem is, nevertheless, not valid for A_3C_{60}.

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Latex-file available from: gunnar@radix3.mpi-stuttgart.mpg.de

Exact Muffin-Tin Orbital Theory

O.K. Andersen, O. Jepsen, and G. Krier
Max-Planck Institut für Festkörperforschung,
D-70569 Stuttgart, Federal Republic of Germany

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Corrections to Migdal's theorem for photoemission spectra

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung,
D-70506 Stuttgart,Germany
V. Meden and K. Schönhammer
Institut für Theoretische Physik,
Universität Göttingen,
D-37073 Göttingen, Germany

Abstract

The electron spectral function is calculated for a model including electron-phonon coupling to Einstein phonons, to study corrections to Migdal's theorem. A cumulant expansion is used for the time-dependent Green's function, and the second and fourth order cumulants are studied. For a one-band model it is illustrated that Migdal's theorem is valid in the large band width limit for a fixed coupling constant. In this limit, the spectrum has at most one satellite in addition to the main peak. As the band width is reduced, the spectrum calculated with the fourth order cumulant develops multiple satellites, if ε_k is close to the Fermi energy. Although the interband electron-phonon coupling is shown to be substantial, and the effective band width may therefore be argued to be large, it is shown that Migdal's theorem is nevertheless not valid for C_{60}.

(to appear in H. Kuzmany, J. Fink, M. Mehring, S. Roth (Eds.),
Electronic Properties of Fullerenes, Proceedings of the International
Winterschool on Electronic Properties of Novel Materials
Kirchberg, Tirol, March 1994,Springer-Verlag)
Latex-file available from: gunnar@radix3.mpi-stuttgart.mpg.de

Fermi surface, bonding, and pseudogap in $MoSi_2$

O.K. Andersen, O. Jepsen, Vl.N. Antonov
Max-Planck Institut für Festkörperforschung,
D-70569 Stuttgart, Federal Republic of Germany
V.N. Antonov, B.Yu. Yavorsky, A.Ya. Perlov, A.P. Shpak
Institute of Metal Physics, Kiev 142, Ukraine

Abstract

The electronic structure and Fermi surface of molybdenum disilicide has been calculated using local density functional theory (LDA) and the linear muffin-tin orbital method (LMTO). The energy bands are analysed in detail for their orbital character. Our explanation for the presence of a pseudo gap after the 7'th band is that the two Si s bands lie low and that there are five Mo d – Si p pair bands. The configuration is approximately Mo $4d^5$ Si_2 $3s^2 3p^{2.5}$. An explanation in terms of directed bond-orbitals was not achieved. The calculated angular dependence of the extremal Fermi surface cross-section areas are in good qualitative agreement with de Haas-van Alphen (dHvA) measurements. However, in order to obtain quantitative agreement, the Mo $d_{x^2-y^2}$ orbital energy has to be shifted upwards by 0.41eV and the Mo d_{xy} energy downwards by 0.20eV. This deficiency is ascribed to the use of a local exchange-correlation potential.

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Latex-file available from: jepsen@radix1.mpi-stuttgart.mpg.de

A quantitative model for the superconductivity suppression in $RE_{1-x}Pr_xBa_2Cu_3O_7$ with different rare earths

A.I. Liechtenstein and I.I. Mazin
Max-Planck-Institut für Festkörperforschung,
Heisenbergstr.1, D-70569 Stuttgart, FRG

Abstract

We report first-principle calculations of the electronic structure of $ABa_2Cu_3O_7$, (A=Pr, Nd), which explicitly take into account the on-site Coulomb correlations in the f-shell of the rare-earth ions. It appears that for A=Pr an additional band crosses the Fermi level, grabbing holes from the (super)conducting $pd\sigma$ band. For A=Nd this band remains completely filled, thus explaining the absence of T_c suppression. On doping $RE Ba_2Cu_3O_7$ with Pr the position of the hole-depleting band depends crucially of the atomic number of the host rare earth, through the position of its f-band. This makes T_c supression in doped compounds different for different hosts, the stronger the smaller the atomic number of the host is. This also provides a natural explanation of the fact that squeezing the cell by external pressure reduces T_c in doped compunds, although the effect of the "chemical pressure" (substituting one RE by another with a smaller size) is opposite. The electrons in the hole-depleting band itself are localized (despite of the considerable band width), because of the strong scattering due to disorder on the RE site.

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

The Stabilization of the Rb^- Anion in $Na_{16}Rb_7Sb_7 = Na_{16}(RbRb_6)Sb_7$**

H.G. von Schnering*, R. Cardoso Gil, W. Hönle, Armin Burkhardt*,
Georges Krier and Ole Krogh Andersen

Dedicated to Professor Manuel Cardona on his 60th Birthday

Abstract

The Zintl phase $Na_{16}Rb_7Sb_7$ is formed directly from the elements. In the structure the rubidium atoms build up two–electron clusters $(RbRb_6)^{5+}$ in which a central Rb^- is stabilized by six octahedrally coordinating Rb^+ cations. *Ab–initio* band structure calculations prove the existence of $(RbRb_6)^{5+}$.

* Prof.Dr. H.G. von Schnering, Dr. R. Cardoso Gil, Dr. W. Hönle
Dr. A. Burkhardt, Dr. G. Krier, Prof.Dr. O.K. Andersen
Stuttgart, Max-Planck-Institut für Festkörperforschung,
Heisenbergstraße 1
70569 Stuttgart

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(accepted to Angew. Chem.)
Latex-file available from: burkhard@radix2.mpi-stuttgart.mpg.de

s-wave superconductivity from antiferromagnetic spin-fluctuation model for bilayer materials

A.I.Liechtenstein[a], I.I. Mazin[a,b], and O.K. Andersen[a]
[a]Max-Planck-Institut für Festkörperforschung,
Heisenbergstr.1, D-70569 Stuttgart, FRG.
[b]Geophysical Laboratory, Carnegie Institution of Washington,
5251 Broad Branch Rd., NW, Washington, DC 20015

Abstract

It is usually believed that the spin-fluctuation mechanism for high-temperature superconductivity results in d-wave pairing, and that it is destructive for the conventional phonon-mediated pairing. We show that in bilayer materials, due to nearly perfect antiferromagnetic spin correlations between the planes, the stronger instability seems to be with respect to a superconducting state whose order parameters in the even and odd plane-bands have opposite signs, while having both two-dimensional s-symmetry, that is, it has three-dimensional p_z-symmetry. The interaction of electrons with Raman-(infra-red) active phonons enhances (suppresses) the instability.

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

Stationary nature of the density functional free energy: application to accelerated multiple scattering calculations

D. M. C. Nicholson, G. M. Stocks, Y. Wang, W. A. Shelton
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114
Z. Szotek, W. M. Temmerman
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Abstract

The number of operations required for conventional Density functional algorithms grows as the cube of the number of atoms, N. For large systems the computing requirements are unattainable. To overcome this limitation it is acceptable to approximate only those variables with respect to which the free energy is stationary. We show that the stationarity of the free energy with respect to electron density, one electron potential, chemical potential, occupation function, and temperature, allow for very useful approximations leading to rapid and accurate determination of the free energy. Here we discuss approximations involved in calculating the finite temperature electron density needed to evaluate the Harris-Foulkes free energy. Of particular importance are: (1) an electron density at each site that is based on exact solution of the Poisson equation combined with a solution of the multiple scattering problem in which only scattering from a small cluster of sites surrounding the site in question is retained and (2) an approximate occupation function having a finite number of poles in the complex energy plane. The intention is to develop, within density functional theory, an $O(N)$ scalable first-principles scheme, based on spatially local multiple scattering methods, for calculating free energies of large systems.

(accepted to Phys. Rev. B (Rapid Commun.))
Latex-file available from: dmn@dmnws.ms.ornl.gov

Local density calculations for large systems using multiple scattering theory

D. M. C. Nicholson, G. M. Stocks, Y. Wang, W. A. Shelton
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114
Z. Szotek, W. M. Temmerman
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Abstract

The accuracy of energy differences calculated from first principles within the local density approximation (LDA) has been demonstrated for a large number of systems. Armed with these energy differences researchers are addressing questions of phase stability and structural relaxation. However, these techniques are very computationally intensive and are therefore not being used for the simulation of large complex systems. Many of the methods for solving the Kohn-Sham equations of the LDA rely on basis set methods for solution of the Schrödinger equation. An alternative approach is multiple scattering theory (MST). We feel that the locally exact solutions of the Schrödinger equation which are at the heart of the multiple scattering method give the method an efficiency which cannot be ignored in the search for methods with which to attack large systems. Furthermore, the analytic properties of the Green function which is determined directly in MST result in computational shortcuts.

(submitted to Surface Review and Letters (World Scientific, Singapore))
Latex-file available from: dmn@dmnws.ms.ornl.gov

Theoretical identification of a (2×2) composite double layer ordered surface alloy of Na on Al (111)

Cathrine Stampfl and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, D-14 195 Berlin-Dahlem, Germany

Abstract

We performed density-functional theory calculations to investigate the (2×2) surface structure of Na on Al (111). This structure forms at room temperature and contains two Na atoms in the surface unit cell. Experiments have surprisingly indicated a strong intermixing of Na and Al in the surface region. ¿From the calculations we predict that the stable geometry is an unusual composite double layer ordered surface alloy where the first Na atom in the surface unit cell occupies a substitutional site and the second Na atom and an Al atom are situated in threefold fcc- and hcp-hollow sites respectively.

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LATEX version can be obtained from: cts@theo21.RZ-Berlin.MPG.DE

Poisoning of Pd(100) for the Dissociation of H_2: A Theoretical Study of Co-adsorption of Hydrogen and Sulfur

Steffen Wilke and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, D-14 195 Berlin-Dahlem, Germany

Abstract

The presence of sulfur adatoms on Pd(100) is known to hinder the dissociative adsorption of hydrogen. Using density-functional theory we studied the adsorption of hydrogen on clean and sulfur precovered Pd(100) surfaces. The results show that the poisoning effect of sulfur is not caused by a strict blocking of hydrogen adsorption sites in the vicinity of S adatoms. For a (2×2) sulfur adlayer (coverage Θ_S =1/4) hydrogen adsorption remains an exothermic process for all surface hollow sites not occupied by sulfur. The blocking of hydrogen adsorption happens only for higher sulfur coverages. We conclude that the poisoning of Pd(100) is a combined effect of the formation of energy barriers hampering the H_2 dissociation *and* a modest decrease of the adsorption energy in the vicinity of the sulfur adatoms.

(Submitted to Phys. Rev. Lett.)
REVTEX version can be obtained from: wilke@theo21.RZ-Berlin.MPG.DE

Theory of Lithium Islands and Monolayers: Electronic Structure and Stability

Sven Quassowski and Klaus Hermann
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, D-14 195 Berlin-Dahlem, Germany

Abstract

Systematic calculations on planar clusters and monolayers of lithium are performed to study geometries and stabilities of the clusters as well as their convergence behavior with increasing cluster size. The calculations are based on ab initio methods using density functional theory within the local spin density approximation for exchange and correlation. The optimized nearest neighbor distances d_{nn} of the Li_n clusters, $n = 1, ...25$, of both hexagonal and square geometry increase with cluster size converging quite rapidly towards the monolayer results. Further, the cluster cohesive energies E_c increase with cluster size and converge towards the respective monolayer values which form upper bounds. Clusters of hexagonal geometry are found to be more stable than square clusters of comparable size in consistence with the monolayer results. The size dependence of the cluster cohesive energies can be described approximately by a coordination model based on the concept of pairwise additive nearest neighbor binding. This indicates that the average binding in the Li_n clusters and their relative stabilities can be explained by simple geometric effects which derive from the nearest neighbor coordination.

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REVTEX version can be obtained from: quassowski@FHI-Berlin.MPG.DE