Ψ_k Newsletter

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

Number 27   June 1998

Contents

1   Editorial

In this Newsletter, in the **TMR1** section, we have a report on the **'Spectroscopy Workshop in Munich'** where the abstracts of all presented papers are included. The job announcements are placed in the **'General Job Announcements'** section, but there is also one announcement in the **TMR2** section, of interest to the EU nationals only. The **Scientific Highlight of the Month** by Ali Alavi et al. is on **'Reaction Pathway for CO oxidation on Pt(111) from ab initio Density Functional Theory'**. Please note that due to large size and complicated figures, they have been placed on the web at:
http://titus.phy.qub.ac.uk/group/Ali/pubs9596.html.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:
http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

The above contains pointers to several other nodes: *O.K. Andersen (Stuttgart), P. Blöchl (IBM, Zürich), M. Gillan (Keele), E.K.U. Gross (Univ. Würzburg), B.L. Györffy (Bri stol), V. Heine (Univ. Cambridge), R. Jones (Univ. Exeter), J. Kübler (TH, Darmstadt), J.L. Martins (IN-ESC, LISBON), R. Nieminen (TU, Helsinki), J. Nørskov (TU, Lyngby)* with information on CAMP, *M. Scheffler (FHI Berlin), K.-H. Schwarz (TU, Vienn a), G.P. Srivastava (Univ. Exeter)*, and *A. Walker (UEA Norwich)*. There are also pointers to the WWW home page of the Solid State Theory Group at National Renewable Energy Laboratory, Golden, CO 80401 *(http://www.sst.nrel.gov)*, and to the home page of Prof. David Vanderbilt, Department of Physics and Astronomy, Rutgers University *http://www.physics.rutgers.edu/ dhv*. If you maintain a home page on your activities we will be happy to include a pointer fro m the *Networks'* home page to your home page.

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

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

	function
psik-coord@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

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

2 General News

As mentioned in previous newsletters, the Psi-k Newsletter is the official communication and report vehicle for the TMR1 and TMR2 Networks, and the ESF Psi-k Community Programme. There are dedicated sections in the newsletter containing interesting and important information on the scientific activities of the networks. We would like to encourage all our readers to view those sections. But we also have general sections for all contributions from outside the networks which would be of interest to the community as a whole. We are very happy to publish in the Psi-k Newsletter any scientific and general information, be it the conference/workshop or position announcements, scientific highlights and abstracts. As before, we would welcome reports on collaborative visits, workshops and conferences, and anything that can increase our scientific awareness in the field. Please do not hesitate to send us any information that could be useful and of interest to the community.

3 News from the TMR1 Network

3.1 Report on Workshop on Spectroscopy

TMR-Network on 'Interface Magnetism'

München, April 24th – 26th, 1998

Organised by: **Hubert Ebert** (he@gaia.phys.chemie.uni-muenchen.de)

The workshop was held at the Institute for Physical Chemistry of the Ludwig-Maximilians-University in München from Friday April 24th until Sunday April 26th. It was organised by H. Ebert and was sponsored by the TMR-Network on 'Interface Magnetism'. One of the major goals of the workshop was to strengthen the interaction and collaboration of the groups working within the TMR-network on spectroscopy with experimental groups active in that field. Accordingly the workshop was attended by 25 participants coming from the TMR-network and by 11 participants coming from outside. Most of the latter ones are members of the network *Zirkular polarisierte Synchrotronstrahlung: Dichroismus, Magnetismus und Spinorientierung* run by the German Federal Ministry for Research and Technology.

Apart from three contributions (Carbone, *Spectroscopy studies of magnetic and quantum size effects in two-dimensional systems*; Ernst, *Real-space non-relativistic angle-resolved photoemission*; Popescu, *Spin-resolved APS investigations on Fe on Cu and Fe on W*) all other contributions were dealing with spin-orbit influenced spectroscopies of magnetic solids, i.e. with magnetic dichroism, clearly indicating that this is still a major issue. The two contributions dealing with the magneto-optical Kerr-effect discussed the effect of lattice distortions (Delin) and introduced the concept of the layer-resolved optical conductivity (Ebert). Work on the magnetic dichroism in the spin- and angular-resolved valence-band photoemission was presented by Rampe and Henk. This was complemented by Hillebrecht's contribution on core level photoemission of ferromagnets. By far most of the talks were dealing with magnetic dichroism in x-ray absorption (Galanakis, *Calculated Circular Magnetic X-ray Dichroism of Fe nitrides and Cu/Fe (001) surfaces*; van der Laan, *Relation between the angular dependence of magnetic x-ray dichroism and anisotropic ground state properties*; Grange, *Magnetocrystalline anisotropy in CoPt$_3$ thin films probed by x-ray magnetic circular dichroism*; Kuch, *Artificial magnetic ordered FeCu alloy thin films on Cu(001): Spin-resolved electronic properties and magnetic dichroism*). Corresponding investigations in the EXAFS regime have been presented by Baberschke (*Magnetic L-edge EXAFS at 3d Elements: Multiple Scattering Analysis and Spin Dynamics*), Popescu (*Interpretation of magnetic EXAFS-spectra on the basis of the MCXD sum rules*), and Jenkins (*Magnetic circular dichroism in Gadolinium metal: The L edges*). Application of the magnetic dichroism

in x-ray absorption for domain imaging has been presented by Fischer. The dichroism in a complementary type of spectroscopy has been discussed by Pustogowa with the contribution on *Spin-polarised relativistic XES for ordered and disordered semi-infinite systems*. Finally, a fully relativistic approach to account for the influence of spin-orbit coupling in the case of spin-resolved AES was presented by Szunyogh.

Altogether it was a meeting with many interesting and stimulating contributions. The lively discussions clearly indicated that the workshop – as intended – increased the interaction between theory and experiment.

<div align="right">(Hubert Ebert)</div>

PROGRAM:

Friday, April 24th, 1998

Afternoon session:
Chair-person: P. Weinberger

14.00		**Opening**		
14.05	14.50	Magnetic linear dichroism in valence-band photoemission of Fe(110) and Magnetic circular dichroism of an interface state of Pd on Co(0001)	A. Rampe	Aachen
14.50	15.45	Magnetic dichroism in off-normal valence-band photoemission	J. Henk	Uppsala
15.45	16.15	**Coffee break**		
16.15	17.00	Spectroscopy studies of magnetic and quantum size effects in two-dimensional systems	C. Carbone	Jülich
17.00	17.45	Real-space non-relativistic angle-resolved photoemission	A. Ernst	Daresbury
17.45	18.15	Spin-resolved Appearance Potential Spectroscopy for transition metal systems	V. Popescu	München

Saturday, April 25th, 1998

Morning session:
Chair-person: H. U. Hillebrecht

9.00	9.30	Calculation of MOKE spectra for 3d elements for 3d elements and compounds with the full-potential LMTO method	A. Delin	Uppsala
9.30	10.15	Calculation of the layer-resolved optical conductivity for magnetic multilayers and surface layer systems	H. Ebert	München
10.15	10.45	**Coffee break**		
10.45	11.20	Calculated circular magnetic x-ray dichroism of Fe nitrides and Cu/Fe (001) surfaces	I. Galanakis	Strasbourg
11.20	12.05	Relation between the angular dependence of magnetic x-ray dichroism and anisotropic ground state properties	G. van der Laan	Daresbury
12.05	14.00	**Lunch**		

Afternoon session:
Chair-person: W. M. Temmerman

14.00	14.45	Magnetic L–edge EXAFS at 3d Elements: Multiple Scattering Analysis and Spin Dynamics	K. Baberschke	Berlin
14.45	15.30	Spin-polarized relativistic XES for ordered and disordered semi-infinite systems	U. Pustogowa	Wien
15.30	16.00	**Coffee break**		
16.00	16.45	Spin-resolved magnetic circular dichroism in core level photoemission of ferromagnets	H. U. Hillebrecht	Düsseldorf
16.45	17.30	Spin-polarized relativistic AES for ordered and disordered semi-infinite systems	L. Szunyogh	Wien
17.30	18.05	Magnetocrystalline anisotropy in $CoPt_3$ thin films probed by x-ray magnetic circular dichroism	W. Grange	Strasbourg
20.00		**Joint dinner**		

Sunday, April 26th, 1998

Morning session:
Chair-person: K. Baberschke

9.00	9.45	Imaging of magnetic domains with magnetic transmission x-ray microscopy	P. Fischer	Würzburg
9.45	10.15	Interpretation of magnetic EXAFS-spectra on the basis of the MCXD sum rules	V. Popescu	München
10.15	10.45	**Coffee break**		
10.45	11.30	Artificial magnetic ordered FeCu alloy thin films on Cu(001): Spin-resolved electronic properties and magnetic dichroism	W. Kuch	Halle
11.30	12.00	Magnetic circular dichroism in Gadolinium metal: The L edges.	A. C. Jenkins	Daresbury
12.00	12.05	**Closing**		
12.05	14.00	**Lunch**		

Magnetic linear dichroism in valence-band photoemission of Fe(110) and Magnetic circular dichroism of an interface state of Pd on Co(0001)

A. Rampe and G. Güntherodt

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Abstract

Magnetic linear dichroism (MLD) in angle-resolved valence-band photoemission of Fe(110) has been investigated by means of symmetry considerations, analytical theory, numerical calculations and photoemission measurements. The dichroic photoemission spectra and their dependence on photon energy clearly show that the microscopic origin of MLD is an interference effect induced by hybridization of initial states of different spatial symmetry at band gaps arising from spin-orbit coupling. The dependence of MLD on the light incidence angle evidences that it is substantially influenced by the optical response of the metal, the approximation of which according to classical Fresnel theory is adequate to reproduce our experimental data.

For on atomic layer Pd on Co(0001) a localized electronic state is observed which exhibits an exchange interaction [1]. By means of magnetic circular dichroism in valence-band photoemission we are able to show that this state possesses additionally a significant spin-orbit interaction.

[1] W. Weber et al., PRB **46**, 6199 (1992).

Magnetic dichroism in off-normal valence-band photoemission

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Abstract

Magnetic dichroism in off-normal photoemission from valence bands of ferromagnets is studied by both symmetry considerations and numerical relativistic calculations. In general set-ups (light polarization, incidence and emission directions, magnetization direction), dichroism is either due to change of the light polarization or due to magnetization reversal, or due to both. Relations between photoemission intensities for different set-ups lead to the definition of asymmetries in order to probe the origin of the dichroism. Numerical relativistic photoemission calculations provide quantitative results for prototypical systems: Ni/Cu(001) with perpendicular magnetization, Co/Cu(001) with in-plane magnetization, and non-magnetic Cu(001).

Spectroscopy studies of magnetic and quantum size effects in two-dimensional systems

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Abstract

Ultrathin films and multilayers represent a new class of magnetic materials with both technological and fundamental relevance. These systems exhibit distinct magnetic properties that derive from reduced dimensionality, lowered atomic coordination and modified atomic geometry. Spectroscopic methods based on spin-dependent photoexcitations provide a ground for the microscopic description of two-dimensional magnetic systems. Examples will be presented from recent photoemission and dichroism studies in Jülich onfinite-size and surface effects in fcc magnetic films, alloys and multilayers.

Real-space non-relativistic angle-resolved photoemission

A. Ernst, W. M. Temmerman, Z. Szotek, and P. J. Durham

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Abstract

A real-space non-relativistic angle-resolved photoemission code has been developed in the independent particle approximation. The method is formulated in terms of the multiple scattering theory using a real-space representation of the Green's function. The advantage of this approach is in the simplification of the study of complex solids. The Green's functions are calculated in the following two ways. The first one is a real-space cluster method to obtain the τ-matrix. This method is simple at the expense of accuracy due to the finite size of the KKR-matrix, which can lead to errors in the contribution from atoms lying far away from the center of the cluster. The convergence is determined by the size of the KKR-matrix, that can be inverted for the calculation of the photocurrent. The other approach is the calculation of the Fourier transformed structure constants using two dimensional periodicity. After inversion of the KKR-matrix in the two dimensional k-space the τ-matrix in real-space can be evaluated by the Brillouin zone integration. This KKR-matrix has a substantially smaller size, and can be inverted for a variety of boundary conditions, referring to bulk, surface, *etc.* We illustrate our approach on the example of the angle-resolved photoemission study of Cu.

Calculation of MOKE spectra for 3d elements and compounds with a full-potential LMTO method

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Abstract

We present first-principles calculations of the magneto-optical polar Kerr effect (MOKE) of manganese pnictides and of cubic and tetragonal Fe, Co, and Ni. The calculations have been performed with a full-potential linear muffin-tin orbital (FP-LMTO) method, within the local (spin) density approximation (LDA) to the exchange-correlation part of the density functional. In general, we find good agreement between our calculations and other calculations as well as experimental spectra. The change of the MOKE signal due to tetragonal distortion was seen to be rather small.

Calculation of the layer-resolved optical conductivity for magnetic multilayers and surface layer systems

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Abstract

A scheme is presented that allows to split the optical conductivity tensor for a magnetic multilayer system into contributions stemming from individual atomic layers. It is demonstrated that the layer projected optical conductivity tensor is related to the electronic properties of only some few neighboring layers. This property allows to predict the magneto-optical properties of rather complex systems if the magneto-optical properties of its basic units are known from a calculation for a closely related but simpler system. The use of this approach to investigate the magneto-optical properties of magnetic surface layers on top of a non-magnetic substrate is demonstrated for some transition metal systems. For this purpose a suitable multilayer system is used as a reference system with its magneto-optical properties calculated using the relativistic spin-polarized version of the LMTO-method of band structure calculation.

Calculated circular magnetic x-ray dichroism of Fe nitrides and Cu/Fe (001) surfaces

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Abstract

We have implemented the calculation of the x-ray absorption cross section for left and right circularly polarized x-ray beams within the local-density approximation by means of our all-electron full-relativistic and spin-polarized full-potential linear muffin-tin orbital method. We show that the $L_{2,3}$ circular magnetic x-ray dichroism of Fe, Fe_3N, and Fe_4N compounds scales to a single curve when divided by the local magnetic moment. Sum-rules determine the spin and orbital magnetic moment of iron atoms in these ordered iron nitrides. The Magnetic dichroism of Fe/Cu (001) multilayers at the K edge shows that p states of Cu are spin polarized by the Fe atoms, and that this moment decreases with the thinkness of the Cu layers in good agreement with experiment [1].

[1] S. Pizzini et al, Phys. Rev. Lett. 74, 1470 (1998).

Relation between the angular dependence of magnetic x-ray dichroism and anisotropic ground state properties

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Abstract

The geometrical aspects of x-ray absorption spectroscopy are discussed as a function of the directions of the light polarization and the magnetization with respect to the crystalline axes of the solid. Relations are presented for the angular dependence of the ground state magnetic moments and the polarized core edge absorption signals in the presence of a second-order perturbation by an arbitrary interaction. The example of second-order spin-orbit interaction in transition metals is given in detail. We show the importance of the magneto-crystalline anisotropy and describe a method to measure directly the anisotropy. A special choice of geometry, such as a transverse magnetic field, in combination with the sum rules for magnetic dichroism makes it possible to separate ground state moments which cannot be distinguished in a collinear geometry. We also show that the anisotropy of the lattice can give strong variations in the observed spin to orbital magnetic moment ratio, which previously might have been ascribed to limitations in the application of the sum rules. When the spin-orbit interaction is treated in second-order, the MAE is proportional to the expectation value of the orbital magnetic moment as given by Bruno's model. However, there are additional terms which are related to the spin-subband orbital moment and to the magnetic dipole operator due to the anisotropy of the field of the spin. The latter term accounts for the spin-flip excitations between the exchange split majority and minority spin bands.

Magnetic L–edge EXAFS at 3d Elements: Multiple Scattering Analysis and Spin Dynamics

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Abstract

The magnetic signal at the L-edges of 3d transition metals is larger by an order of magnitude as compared to the K–edge measurements as final d states are probed in the former case. We use two experimental arrangements: polycrystalline Fe, Co films in transmission and Fe, Co epitaxially grown films on Cu(001) measured with electron yield. The amplitude ratio MEXAFS/EXAFS equals $\approx 3\%$. The relative MEXAFS amplitudes of Fe/Co of 1.2 shows the scaling of the MEXAFS amplitudes to the magnetic moments. Single- and multiple scattering contributions are identified and separated. The differences for the spin dependent and spin averaged multiple scattering contributions will be analyzed. Finally we will discuss the temperature dependence of the spin dependent mean square relative displacement. This work was supported by DFG SFB 290 and BMBF (05621 KEA5) grants.

Spin-polarized relativistic XES for ordered and disordered semi-infinite systems

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Abstract

X-ray emission spectroscopy (XES) of a Co monolayer on a Cu(100) substrate capped by a monolayer of various $3d$, $4d$, and $5d$ transition metals are presented in terms of first-principles calculations. Based on spinpolarized fully relativistic multiple scattering theory a theoretical description of valence band XES is used to emphasize new features in comparison to a non-spinpolarized description. In addition, the sensitivity of the spectra to the relative angle between the emission direction and the magnetization of the specific site is shown. Variations in the calculated Co spectra with respect to the cap-layer material are explained by means of electronic structure calculations using the screened Korringa-Kohn-Rostoker method. In particular, different hybridization effects of the cap layer with the Co monolayer as a result of different cap-layer materials are discussed. Characteristic differences in the spectral resolution for left- and right-circular polarized emitted photons (magnetic dichroism) are related to spin-up and spin-down densities of states.

Spin-resolved magnetic circular dichroism in core level photoemission of ferromagnets

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Abstract

Magnetic circular dichroism in core level excitations of the 3d transition metal ferromagnets was studied by high resolution spin-polarized photoemission. The experiment was motivated by the increasing number of detailed theoretical investigations of dichroic core level photoemission from ferromagnets, as well as to provide a basis for a detailed comparison between circular and linear dichroism in transverse geometry for which spin-resolved data are already available. The experiments were performed at the helical undulator beamline of the ESRF, Grenoble. The samples were ultrathin films grown in situ on W(110). For spin analysis, scattering off a magnetized Fe(100) surface was used. For Fe and Co, indications for the presence of a satellite were found, which had been observed already in Fe linear dichroism. By spin analysis, each of the dichroic spectra splits up further in majority and minority spin spectra, from which the so-called fundamental spectra are derived. The exchange polarization is similar for Fe and Co, while the spin-orbit polarization shows significant differences.

Spin-polarized relativistic AES for ordered and disordered semi-infinite systems

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Abstract

We present a spin-polarized relativistic band-structure theory of the Auger-electron spectra. The theory accounts for spin- and angle-resolved intensities, which clearly provide information on the (spin-polarized) electronic structure of a surface of metal. It is stressed that as used in combination with the Screened Korringa–Kohn–Rostoker method and the Coherent Potential Approximation a sensitive tool for probing the surface of disordered systems can be obtained.

Imaging of magnetic domains with magnetic transmission x-ray microscopy

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Abstract

The discovery of X-ray magnetic circular dichroism (X-MCD) has opened a variety of new methods to study magnetic structures with synchrotron radiation. Attractive features of X-MCD are its element- and symmetry-specificity, the direct correlation of the dichroic signal to the local magnetic moment and the possibility to distiguish between spin and orbital contributions to the local magnetic moments.

At $L_{2,3}$ absorption edges in 3d elements the X-MCD yields a strong dependence of the absorption coefficient on the relative orientation of the magnetic moments and the photon propagation direction with values up to 50%. In combination with the Transmission X-ray Microscope (TXM) at BESSY I this could be used as contrast mechanism to image magnetic domains with a high lateral resolution (down to $30 nm$). Special virtues of this new microscopy technique are the insensitivity to the surface and the recording of magnetic images in varying applied magnetic fields. Results obtained with GdFe and PtCo systems of different morphological properties (amorphous and multi-layered systems) are reported. Micromagnetic properties, like nucleation and the density of pinning centers as well as time-dependent effects will be discussed.

Research funded by BMFT 05 621 WAA 6 and 05 644 MGA.

Interpretation of magnetic EXAFS-spectra on the basis of the MCXD sum rules

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Abstract

A fully relativistic theoretical description of magnetic EXAFS (MEXAFS) is presented that has been setup in the framework of relativistic multiple scattering theory on the basis of the Dirac equation for spin-polarised, magnetic solids. This approach is applied to supply a detailed interpretation of new and very accurate experimental data that have been recorded for photon energies up to 600 eV above the Fermi level. In particular it is demonstrated that the MEXAFS spectra for pure elements as well as for complex systems can be interpreted on the basis of the so-called sum rules.

Artificial magnetic ordered FeCu alloy thin films on Cu(001): Spin-resolved electronic properties and magnetic dichroism

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Abstract

Alloys of the otherwise immiscible elements FeCu have been prepared by pulsed laser deposition in the fcc $L1_0$ ordered phase on Cu(100). These films consist of alternatingly stacked monolayers of Fe and Cu. Investigations were performed to study the electronic and magnetic properties of the epitaxial FeCu(100) alloy films. Spin-resolved valence band photoemission measurements show the doubling of the unit cell in the ordered alloy with respect to pure Cu or Fe due to the reduced size of the alloy Brillouin zone perpendicular to the film plane. Element selective electronic and magnetic properties were obtained by magnetic circular dichroism in x-ray absorption spectroscopy at the Fe and Cu $L_{2,3}$ edges. An increase in the number of Cu $3d$ holes with respect to pure Cu leads to induced moments on the Cu sites. Applying sum-rules, under some assumptions the elementally resolved spin and orbital magnetic moments can be calculated from the experimental absorption spectra. We find the orbital moments of the Fe atoms in the FeCu alloys to be significantly enhanced with respect to Fe/Cu(100), whereas the spin moments are about the same.

Magnetic circular dichroism in Gadolinium metal: The L edges

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V. Popescu and H. Ebert
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Abstract

The calculated x-ray absorption and circular magnetic x-ray dichroic spectra for the L_1-, L_2- and L_3- edges of Gadolinium metal are presented. This spectra is compared with available experimental data and reasonable agreement between the two is found. A study of the calculated dichroic signal at the experimental volume indicates that the dichroic signal is not highly sensitive to variation in c/a ratio of the unit cell. The layer-by-layer dichroic signal for a Gadolinium slab is also presented.

4   News from the TMR2 Network

'Electronic Structure calculations of materials properties and processes for industry and basic science'

The TMR2 network has a home page at:
http://da601.dfi.aau.dk/ svane/tmr-psik.htm
and we would like to encourage everybody to view it.

4.1   Job Announcement

POSTDOCTORAL POSITION IN CONDENSED MATTER THEORY

**Institut für Theoretische Physik and
Center for Computational Materials Science
Technische Universität Wien**

A postdoctoral position at the Institut für Theoretische Physik and the Center for Computational Materials Science of the Technische Universität Wien are available within the TMR-Network *Electronic structure calculations of materials properties and processes for industry and basic sciences* . Within this network the partner Austria will be in charge of the subproject *Noncollinear magnetism* and also of the coordination of activities in this area in Darmstadt, Jülich, Warwick, Uppsala and Strasbourg. The applicant should have a thorough background in electronic structure theory, some experience in spin-polarized calculations would be a strong recommendation. Applications are open to EU-nationals (except Austrians) or nationals of an associated state (Norway, Iceland, Israel) only, there is an age limit of 36 years. The salary is equivalent to that of an assistant professor at an Austrian University.

Applications should be adressed to: Professor Juergen Hafner (email: jhafner@tph.tuwien.ac.at, FAX: +43-1-5867760), Institut für Theoretische Physik, Technische UniversitÄt Wien, Wiedner Hauptstrasse 8/10, A-1060 WIEN, Austria.

5 News from the ESF Programme

"Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

5.1 Call for Proposals

Since the contract with the ESF regarding the Psi-k ESF Programme has been finalised, the Psi-k collaborative visits programme has now been restarted. Hereby we want to encourage you to submit proposals for collaborative visits and workshops. The rules of applying for financial support to make a collaborative visit between different scientific institutions in Europe are the same as in the case of the former HCM Ψ_k−Network. One simply needs to submit a small scientific proposal, with an estimate of costs involved, to **psik-management@dl.ac.uk**. The decision approving the visit will be taken within two weeks from submission of the proposal. Please note that only the scientists from the countries which contribute to the Psi-k ESF Programme are eligible for financial support. They are: Austria, Belgium, Denmark, Finland, France, Germany, Hungary, Ireland, Italy, Poland, Portugal, Slovenia, Sweden, Switzerland and UK.

The first important event of the ESF Psi-k Programme is the **Industry Workshop** in Vienna on June 3-4, 1998, jointly organized with the TMR2 Network. The latest information on this, including the programme of the workshop, can be found at: **http://tph.tuwien.ac.at/psik/**.

6   General Job Announcements

Two (up to) 5-years Post-doc Positions
at the
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

We have openings for two post-doc positions. Each position is at first for one year, but a prolongation is possible. The maximum duration is 5 years. The projects are:

1) Chemical reactions of simple molecules at transition metal surfaces (in the ground state and electronically excited states). The project will involve detailed density functional theory calculations of the high-dimensional potential-energy surface, ab initio molecular dynamics, time-dependent DFT, and GW calculations.

2) Ab initio Kinetic Monte Carlo (KMC) calculations of crystal growth and the formation of nano-scale structures at surfaces (semiconductor quantum dots and magnetic metal islands). The KMC input (energy barriers, attempt frequencies) are to be determined by detailed ab initio molecular dynamics calculations.

Applicants should have experience in some (not necessarily all) of the mentioned methods. Details about the group and some research projects can be found at

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and
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Applications should be sent by e-mail as a postscript file or on paper by normal mail to:

Matthias Scheffler
Fritz-Haber-Institut der MPG
Faradayweg 4-6
D-14195 Berlin-Dahlem
Germany

email: scheffler@fhi-berlin.mpg.de

UNIVERSITY OF DUBLIN TRINITY COLLEGE
Department of Chemistry
Department of Physics
LECTURER IN COMPUTATIONAL CHEMISTRY or COMPUTATIONAL PHYSICS

Applications are invited for the above post which will be tenable from 1st October 1998 and will be made on contract for up to five years.

The successful applicant will be involved in designing and teaching two innovative undergraduate degree courses in Computational Chemistry and Computational Physics. The most important qualification for this position will be a demonstrable ability for high quality research in some area of Computational Chemistry or Physics which complements current research in the Departments. Candidates should include a short (two page maximum) outline research proposal. Researchers in the College use a high performance computer (currently a 48 node, 27 GigaFLOPS peak IBM SP2 parallel computer) at the Centre for Supercomputing in Ireland.

Salary Scales:
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15,080 - 23,767 (Irish pounds)
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Appointment will be made on the Lecturer Grade II scale (equivalent to Assistant Professor in the USA/Canada) at a point to accord with the qualifications and experience of the successful candidate. Prof. John Corish in Chemistry, jcorish@tcd.ie, or Prof. Denis Weaire in Physics, dweaire@tcd.ie, may also be approached for additional information. The closing date for receipt of completed applications will be Thursday, 4th June, 1998. Application forms and further particulars relating to this post may be obtained from:

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Ph. D. Position in Computational Solid State Physics

Swiss Federal Institute of Technology, Lausanne, Switzerland

A Ph. D. position is available at the Laboratoire de Théorie du Solide (Institute of Applied Physics) in the group of Prof. A. Baldereschi. A prospective student will be expected to investigate, using ab–initio calculations, dielectric and structural properties of mixed ionic/covalent materials. In particular, he/she will study the microscopic mechanisms leading to large dynamical charges and structure instabilities in some important classes of transition metal oxides. The applicant should have good knowledge of theoretical solid state physics and chemistry, and experience with the handling of large computer codes and modern scientific programming.

The position is expected to start immediately, or upon mutual agreement. Interested candidates are invited to submit their curriculum vitae, together with two letters of reference and any other relevant documents to:

Dr. M. Posternak
Ecole Polytechnique Fédérale
Institut de Physique Appliquée, Laboratoire de théorie du solide
PH–Ecublens, CH–1015 Lausanne, Switzerland
e–mail: postma@dpmail.epfl.ch
fax: (+41 21) 693 4444
phone: (+41 21) 693 4435

Further information can be obtained at the same address.

Postgraduate opportunity in quantum mechanical modelling of defects in solids at University College London

The Condensed Matter and Materials Physics group at the Department of Physics and Astronomy UCL welcomes applications from outstanding EU and overseas students for postgraduate studies in this leading group. The project is funded by an industrial company who, irrespective of nationality, will pay full student fees and maintenance. The funds are provided on yearly basis and are subject to successful completion of the previous years' scientific programme, and on the economic status of the industrial sponsor.

The project involves the development and application of quantum mechanical methods and computer codes for quantitative modelling of defects and defect processes in polar crystals and amorphous materials. Successful applicant should have knowledge of quantum-chemical and solid state methods of many-electron calculations, experience in their applications to molecules or solids, and proven programming skills. Good command of mathematical physics is an advantage.

Please send your applications by June 15, 1998 to Dr. Alex Shluger at A.Shluger@ucl.ac.uk, or by post to **Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK**; tel. 44-171-391 1312. Promising applicants will be required to attend an interview.

Post-doctoral Position, Condensed Matter Theory Computational Materilas Theory Center California State University Northridge

One or two postdoc and/or visiting positions and one graduate student position are available with the Computational Materials Theory Center at California State University Northridge, starting immedaitely. The position is available for one year and may be extended for up to two years subject to availablility of funding. Our main activities are centered on the application and development of electronic structure methods. Specific projects concern electronic structure calculations for the determination of mechanical properties, magnetism in rare-earth and actindes, surface magnetism and magnetooptics and surface catalysis. Quantum Molecular Dynamics and Monte Carlo simulations as applied to these and other systems are also of interest.

The candidate should have experience with density functional electronic structure calculations and/or quantum molecular dynamics calculations.

The Computational Materials Theroy Center consists of three faculty, four postdoctoral fellows, one visiting fellow, and several graduate students.

Interested persons should send their resumes and the names of references preferably via e-mail, as soon as possible.

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7   Abstracts

Magnetic impurity states in simple metals: a study of the spin-polarization energy

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Panepistimioupolis, GR-157 84 Zografos, Athens, Greece

Abstract

We report a systematic study of the spin-polarization energy of $3d$ impurities in monovalent simple-metal hosts, by means of self-consistent, local-spin-density-functional, impurity-in-jellium calculations, and propose a phenomenological model for the interpretation of our results.

Effective single-particle potentials for MnO: present status and perspectives in the light of analysis of inter-atomic magnetic interactions

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Abstract

It is shown that the fundamental gauge-symmetry constraints superimposed on the admissible form of the exchange-correlation energy functional lead to the generalized local force theorem for small non-uniform rotations of the spin magnetic moments near an equilibrium. The theorem suggests that the magnetic interactions responsible for the low-energy spin-wave excitations near the ground state can be expressed in terms of the effective single-particle potential designed for the ground-state spin-magnetization density. The theorem allows us to obtain an empirical effective potential for MnO by fitting the experimental low-temperature spin-wave dispersion curve. The theorem is further applied to investigate abilities of several different first principles techniques: local-(spin)-density approximation [L(S)DA], LDA plus "Hubbard U" (LDA+U) and Optimized Effective Potential (OEP). None of these approaches treats the magnetic interactions in MnO properly. Limitations of the one-electron band picture underlying the failure are elucidated in each case. As one of the perspective techniques to deal with the electronic structure of narrow-band materials, we propose to combine the LDA+U form of the single-particle equations with the variational principles of the OEP approach. Several possible approximations along this line are discussed.

The GW method

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Abstract

Calculations of ground-state and excited-state properties of materials have been one of the major goals of condensed matter physics. Ground-state properties of solids have been extensively investigated for several decades within the standard density functional theory. Excited state properties, on the other hand, were relatively unexplored in *ab initio* calculations until a decade ago. The most suitable approach up to now for studying excited-state properties of extended systems is the Green function method. To calculate the Green function one requires the self-energy operator which is non-local and energy dependent. In this article we describe the *GW* approximation which has turned out to be a fruitful approximation to the self-energy. The Green function theory, numerical methods for carrying out the self-energy calculations, simplified schemes, and applications to various systems are described. Self-consistency issue and new developments beyond the *GW* approximation are also discussed as well as the success and shortcomings of the *GW* approximation.

Mott transition and superconductivity in alkali-doped fullerides

O. Gunnarsson, E. Koch and R.M. Martin

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Department of Physics, University of Illinois, Urbana, Illinois 61801

Abstract

We study the effects of deviations from cubic symmetry on superconductivity and on Mott transitions by comparing A_3C_{60} and $NH_3K_3C_{60}$. The reduced frustration in $NH_3K_3C_{60}$ favours a Mott transition at a lower ratio U/W, where U is the Coulomb repulsion of two electrons on the same molecule and W is the width of the t_{1u} band. The closeness of $NH_3K_3C_{60}$ to a Mott transition may influence the superconductivity negatively, due to an inefficient screening of the Coulomb repulsion.

Dielectric screening in doped Fullerides

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Department of Physics, University of Illinois, Urbana, IL

Abstract

For conventional superconductors the electron-electron interaction is strongly reduced by retardation effects, making the formation of Cooper pairs possible. In the alkali-doped Fullerides, however, there are no strong retardation effects. But dielectric screening can reduce the electron-electron interaction sufficiently, *if* we assume that the random-phase approximation (RPA) is valid. It is not clear, however, if this assumption holds, since the alkali-doped Fullerides are strongly correlated systems close to a Mott transition. To test the validity of the RPA for these systems we have calculated the screening of a test charge using quantum Monte Carlo.

Noncollinear magnetism in itinerant electron systems: Theory and applications

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Abstract

The article attempts to review the present stage of the density functional theory (DFT) for noncollinear magnetic states and its application to particular physical problems. The discussion starts with basic theorems of the theory and derivation of the Kohn-Sham equation for a noncollinear magnet. Special features of solving this equation are illustrated using the augmented spherical wave method generalized to the noncollinear magnetic structures as an example. Particular attention is devoted to the symmetry of the problem. It is shown that a traditional approach of the space group theory fails in the case of a noncollinear magnetic state. A generalized approach based on the notion of the spin-space groups is presented which allows a consequent treatment of the symmetry properties of both non-relativistic and relativistic problems. This approach allows to develop an exact procedure for a first-principle calculation of an incommensurate spiral structure and gives a sound basis for the calculation and physical interpretation of the noncollinear magnetic structures caused by the effects of relativity. Application of the theory to the first principle determination of the complex noncollinear magnetic structures of various systems are discussed. Applications include the spiral structure of fcc-Fe, the uncompensated magnetic structure in U_3X_4 and compensated magnetic structure in U_2P_2Sn, and two different types of weak ferromagnetism in Fe_2O_3 and Mn_3Sn. It is shown how the calculation technique can be applied to studies of unenhanced and enhanced non-uniform magnetic susceptibilities as well as susceptibilities in fields noncollinear to the atomic moments. Illustrating results of the calculation of the susceptibility of various systems are presented. The last part of the review is devoted to applications of the theory of noncollinear magnetism to studies of temperature effects in the electronic properties of itinerant magnets.

Magnetism of UT_2Si_2 compounds: effect of the orbital polarization correction

A. Mavromaras, L.M. Sandratskii and J. Kübler

Institut für Festkörperphysik, Technische Universität,

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Abstract

Two different ways to deal with correlations in localized f-electron systems in the framework of local spin density functional theory are compared, using new calculations for the series of uranium intermetal lic compounds UT_2Si_2 (T=Cr,Mn,Fe,Co,Ni,Cu,Ru,Rh,Pd,Os). The strong localization and hence atomic like behaviour of the Uranium 5f-states is taken into account by incorporation of Hund's second rule through an orbital polarization correction (OPC) field. The two OPC methods tested are the L^2 method and the Orbital Hartree Fock method . Results for electronic and magnetic ground-state properties are compared with previous calculations based on spin-orbit coupling (SOC), as well as with experimental data. Both methods are found to yield a considerable improvement of the theoretical value of the magnetic moments over standard spinpolarized density functional calculations. Furthermore, other aspects such as the impact of the OPC methods on the calculat ed density of states are discussed.

Optical Properties of U_3P_4

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Abstract

Optical and magneto-optical properties of the non-collinear ferromagnet U_3P_4 are studied theoretically over the broad energy range of 0-12 eV. The calculations are carried out in the framework of the local density functional theory treating the U 5f electrons as itinerant, and the results are compared with available experimental data. For low energies, below 5 eV, the agreement between theory and experiment is good. Above 5 eV the theoretical optical characteristics exceed substantially the corresponding experimental values. Possible reasons for this difference are discussed. Much attention is devoted to the role played by the 5f electrons for the formation of the optical properties. To do this we determine the electronic structure and optical properties of Th_3P_4 which, although similar in many respects to U_3P_4, does not possess occupied 5f electrons. Our results for Th_3P_4 are compared with experimental data for Th_3P_4 and theoretical results for U_3P_4 in an attempt to relate the differences in the optical characteristics of both compounds to the effect of the U 5f electrons. By means of a model calculation we extract the contribution of the U 5f states to the optical properties of U_3P_4 and find this contribution to be substantial for energies below $E \approx 3\,\mathrm{eV}$. On the basis of good agreement between theory and experiment in this energy range we infer that in U_3P_4 the U 5f electrons are itinerant. Finally we discuss the influence of the non-collinearity of the magnetic structure on the optical properties of U_3P_4.

Adatom Diffusion at GaN (0001) and (000$\bar{1}$) Surfaces

Tosja Zywietz, Jörg Neugebauer, Matthias Scheffler

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Abstract

The diffusion of Ga and N adatoms has been studied for the technologically relevant wurtzite (000$\bar{1}$) and (0001) surfaces employing density-functional theory. Our calculations reveal a very different diffusivity for Ga and N adatoms on the equilibrium surfaces: While Ga is very mobile at typical growth temperatures, the diffusion of N is by orders of magnitudes slower. These results give a very detailed insight of how and under which growth conditions N adatoms can be stabilized and efficiently incorporated at the surface. We further find that the presence of excess N strongly increases the Ga diffusion barrier and discuss the consequences for the growth of GaN.

The Dynamics of the H + D/Si(001) reaction: A Trajectory study based on *ab initio* Potentials

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Abstract

The adiabatic potential energy surface for the reaction of H atoms with the deuterated Si(001) surface is calculated using a slab geometry and spin-polarized density functional theory with gradient corrections. Its dynamical implications are investigated through classical trajectory simulations. A significant probability for the exothermic production of HD molecules is found. In agreement with recent experiments, the kinetic energy of the HD molecules is the most important channel of energy disposal. For larger energies of incidence of the H atoms, molecular and substrate degrees of freedom take up an increasing amount of energy, leading to a broadening of the HD kinetic energy distributions.

Theoretical analysis of the electronic structure of the stable and metastable $c(2 \times 2)$ phases of Na on Al (001): Comparison with angle-resolved ultra-violet photoemission spectra

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[3]*Institut de Physique, Université de Fribourg, Pérolles,*

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Abstract

Using Kohn-Sham wave functions and their energy levels obtained by density-functional-theory total-energy calculations, the electronic structure of the two $c(2 \times 2)$ phases of Na on Al (001) are analysed; namely, the metastable hollow-site structure formed when adsorption takes place at low temperature, and the stable substitutional structure appearing when the substrate is heated thereafter above ca. 180K or when adsorption takes place at room temperature from the beginning. The experimentally obtained two-dimensional band structures of the surface states or resonances are well reproduced by the calculations. With the help of charge density maps it is found that in both phases, two pronounced bands appear as the result of a characteristic coupling between the valence-state band of a free $c(2 \times 2)$-Na monolayer and the surface-state/resonance band of the Al surfaces; that is, the clean (001) surface for the metastable phase and the unstable, reconstructed "vacancy" structure for the stable phase. The higher-lying band, being Na-derived, remains metallic for the unstable phase, whereas it lies completely above the Fermi level for the stable phase, leading to the formation of a surface-state/resonance band-structure resembling the bulk band-structure of an ionic crystal.

Theory of doping and defects in III-V nitrides

C. G. Van de Walle[1], C. Stampfl[2], and J. Neugebauer[2]

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[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
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Abstract

Doping problems in GaN and in AlGaN alloys are addressed on the basis of state-of-the-art first-principles calculations. For n-type doping we find that nitrogen vacancies are too high in energy to be incorporated during growth, but silicon and oxygen readily form donors. The properties of oxygen, including DX-center formation, support it as the main cause of unintentional n-type conductivity. For p-type doping we find that the solubility of Mg is the main factor limiting the hole concentration in GaN. We discuss the beneficial effects of hydrogen during acceptor doping. Compensation of acceptors by nitrogen vacancies may occur, becoming increasingly severe as x increases in $Al_x Ga_{1-x} N$ alloys.

The hematite (α-Fe$_2$O$_3$) (0001) surface: evidence for domains of distinct chemistry

X.-G. Wang, W. Weiss, Sh. K. Shaikhutdinov, M. Ritter,
M. Petersen, F. Wagner, R. Schlögl, and M. Scheffler

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Abstract

Using spin-density functional theory we investigated various possible structures of the hematite (0001) surface. Depending on the ambient oxygen partial pressure, two geometries are found to be particularly stable under thermal equilibrium: one being terminated by iron and the other by oxygen. Both exhibit huge surface relaxations (-57% for the Fe- and -79% for the O-termination) with important consequences for the surface electronic and magnetic properties. With scanning tunneling microscopy we observe two different surface terminations coexisting on single crystalline α-Fe$_2$O$_3$ (0001) films, which were prepared in high oxygen pressures.

Anomalously Large Thermal Expansion at the (0001) Surface of Beryllium without Observable Interlayer Anharmonicity

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M. Scheffler[3], and E. W. Plummer[1a,1b]

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Abstract

We have measured a large thermal surface expansion, 6 times larger than the bulk, on Be(0001) using low-energy electron diffraction. This observation seems to be inconsistent with previous measurements reporting negligible anharmonicity in the surface phonon modes normal to the surface. Density-functional theory calculations for the thermal expansion from the minimum in the free energy within the quasiharmonic approximation agree with the experimental observations and demonstrate that the enhanced thermal expansion is caused largely by a softening of the in-plane vibrations.

The influence of surface stress on the equilibrium shape of strained quantum dots

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Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Abstract

The equilibrium shapes of InAs quantum dots (i.e., dislocation-free, strained islands with sizes < 10 000 atoms) grown on a GaAs (001) substrate are studied using a hybrid approach which combines density functional theory (DFT) calculations of microscopic parameters, surface energies, and surface stresses with elasticity theory for the long-range strain fields and strain relaxations. In particular we report DFT calculations of the surface stresses and analyze the influence of the strain on the surface energies of the various facets of the quantum dot. The surface stresses have been neglected in previous studies. Furthermore, the influence of edge energies on the island shapes is briefly discussed. From the knowledge of the equilibrium shape of these islands, we address the question whether experimentally observed quantum dots correspond to thermal equilibrium structures or if they are a result of the growth kinetics.

Adsorption of CO on Pd(100): steering into less favored adsorption sites

A. Eichler and J. Hafner

Institut für Theoretische Physik

and Center for Computational Materials Science

Technische Universität Wien, Wiedner Hauptstraße 8-10/136,

A-1040 Wien, Austria

Abstract

Molecular steering effects have been shown already in a number of cases to constitute an effective mechanism to avoid barriers and enhance sticking at low incidence energies. We present a study of the adsorption process of CO on the Pd(100) surface, where a similar mechanism leads to trapping of some of the molecules in less favorable surface sites. The electronic charge transfers and redistributions connected with this process are analyzed in detail.

Adsorption of CO on Rh(100) studied by ab-initio local-density-functional calculations

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and Center for Computational Materials Science

Technische Universität Wien, Wiedner Hauptstraße 8-10/136,

A-1040 Wien, Austria

Abstract

Ab-initio local-density-functional studies of the adsorption of CO on the (100) surface of Rh have been performed. We show that although adsorption in the bridge-site is always energetically more favourable than adsorption in either the on-top or the hollow sites, two different mechanisms can lead to a relatively high occupation of the on-top sites: (i) At higher coverage the interactions between the adsorbates stabilize a pseudo-hexagonal coincidence lattice with the experimentally observed $p(4\sqrt{2} \times \sqrt{2})$ structure with a bridge/on-top ratio of 2:1 (all adsorbates being slightly shifted from their high-symmetry positions). (ii) At lower coverages there seems to be a contradiction between the energetic preference for bridge-site adsorption and the mixed top/bridge adsorption reported in the experiments. This could simply be dismissed as a failure of density-functional theory. However, we speculate about a possible way to reconcile the calculated potential energy surface and the experimental observations: At distances larger than 1.75 Åfrom the surface (this is smaller than the equilibrium height for on-top adsorption), the interaction-energy with the on-top site is always larger by $\sim$ 0.5 eV than with the bridge-site. The on-top adsorbed molecule is metastable, because there is a barrier of 0.06 eV for migration to the bridge site and the reaction channel is very narrow. This leads to the observed mixed occupation of top and bridge sites at lower coverage ($\Theta \leq 0.5$).

Molecular precursors in the dissociative adsorption of O_2 on Pt(111)

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and Center for Computational Materials Science
Technische Universität Wien, Wiedner Hauptstraße 8-10/136,
A-1040 Wien, Austria

Abstract

Ab-initio local-spin-density calculations for the adsorption of O_2 on Pt(111) are presented. We identify two distinct, but energetically almost degenerate chemisorbed precursors. A superoxo-like paramagnetic precursor is formed at the bridge-site, with the molecule parallel to the surface. A second peroxo-like nonmagnetic precursor is formed in the threefold hollow, with the atom slightly canted in a top-hollow-bridge geometry. The nature of the barrier for dissociation into atoms adsorbed in the hollows is explored.

The adsorption of thiophene on the catalytically active edge-surface of MoS$_2$: An ab-initio local-density-functional study

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Abstract

The adsorption of thiophene on the catalytically active MoS$_2$(010) edge-surfaces has been studied using ab-initio local-density-functional molecular-dynamics. It is shown that thiophene adsorbs in an η^5-configuration with the molecular ring parallel to the surface, centered above a coordinatively unsaturated Mo-atom, and with the sulfur atom in a binding position between two Mo-surface atoms. This configuration provides not only the highest adsorption energy, but activates in addition the thiophene molecule with respect to both C-S bond-cleavage (and hence desulfurization) and hydrogenation. Hence it represents a realistic scenario for the first step in catalytic hydrodesulfurization.

The adsorption of thiophene on RuS$_2$: an ab-initio density-functional study

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Technische Universität Wien, Wiedner Hauptstraße 8-10/136,
A-1040 Wien, Austria

Abstract

The adsorption of thiophene on stoichiometric and reduced (100) surfaces of RuS$_2$ has been studied using *ab-initio* density-functional molecular dynamics. On the stoichiometric surface, the thiophene molecule is shown to adsorb in a tilted η^1 position where the S atom of the molecule forms a bond with the surface Ru atom similar to that in the bulk RuS$_2$, but there is no activation of the molecule. Formation of sulfur vacancies on the surface creates a chemically active surface and possibility of thiophene adsorption in the η^2 position, where the molecule is activated. These findings are in good agreement with recent experimental evidence of a drastic increase in catalytic activity of the reduced RuS$_2$ surface and should contribute to a better understanding of unique catalytic properties of RuS$_2$ for thiochemistry applications.

Calculated properties of Gadolinium/Molybdenum multilayers

A.C. Jenkins and W.M. Temmerman

CLRC, Daresbury Laboratory, Warrington, Cheshire, UK, WA4 4AD

Abstract

The self-consistent tight-binding linear-muffin-tin-orbital method, with the atomic-sphere-approximation, is used to obtain a description of the magnetic structure of Gadolinium/Molybdenum multilayers. It is found that a large magnetic moment can be induced on the Molybdenum site mainly due to the volume expansion of the spacer in the multilayer. Furthermore Molybdenum is antiferromagnetic and Gadolinium is ferromagnetic within the multilayer. Consequently it may be deduced that the use of Molybdenum as a substrate does not influence the magnetic ordering of Gadolinium as the magnetic ordering of the two materials within the multilayer is identical to that predicted for the bulk.

On the nature of the magnetic coupling at the Gd (0001) surface

A.C. Jenkins and W.M. Temmerman

Daresbury Laboratory, Warrington, Cheshire, UK, WA4 4AD

Abstract

We report on the application of the LSDA and the PBE [1] to the description of the magnetic coupling at the Gd (0001) surface. The first-principles technique employed is the self-consistent LMTO-ASA. We find that the magnetic coupling in bulk Gd is dependent on the interlayer spacing. This observation is used to analyze the nature of the magnetic coupling between the surface and subsurface layers for Gd (0001) for various surface relaxations.

[1] John P. Perdew, Kieron Burke and Matthias Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

8 SCIENTIFIC HIGHLIGHT OF THE MONTH

Reaction Pathway for CO oxidation on Pt(111) from ab initio Density Functional Theory

Ali Alavi [1], Peijun Hu[2], Thierry Deutsch [1*], Pier Luigi Silvestrelli[3] and Jürg Hutter[3]

[1] *Atomistic Simulation Group, School of Mathematics and Physics,*
Queen's University, Belfast BT7 1NN, U.K.

[2] *School of Chemistry, Queen's University, Belfast BT9 5AG, U.K.*

[3] *Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany*

Abstract

CO oxidation on Pt(111) is studied with *ab initio* density functional theory. The low energy pathway and transition state for the reaction are identified. The rate-limiting step is the breaking of an O-metal bond prior to the formation of a chemisorbed CO_2 molecule. The pathway can be rationalised in terms of competition of the O and C atoms for bonding with the underlying surface, and the predominant energetic barrier is the strength of the O-metal bond.

It has been known for a long time [1] that the oxidation of CO can be effectively catalysed by certain transition metals. This phenomenon has since come to prominence both for its intrinsic scientific interest and for its immense technological importance [2]. For example, car exhaust catalytic converters, widely used since the 1970's to remove CO and other pollutants from exhaust emission, have as their active components transition metals such as Pt, Pd or Rh supported on metal oxides. Spurred by such technological interest CO oxidation on transition metal surfaces has become one of the most widely studied catalytic reactions [2, 3, 4, 5]. It remains, however, inadequately understood. In order to provide insight into the development of new catalysts, two important questions can be phrased as follows: (1) What is the transition state in this reaction? (2) What is the physical origin of the reaction barrier? Answers to the second question are crucial since the reaction rate, i.e. the efficiency of the catalyst, decreases exponentially with the energetic barrier, and it is obvious the answer to the first question must be sought before the second can be tackled. In this study we focus on these two issues.

We used a finite temperature formulation of density functional theory [6], using non-local pseudopotentials and a plane wave basis set, as implemented in the code FEMD [7]. In this method,

the self-consistent electronic density is computed using an efficient iterative diagonalisation [8] of a high-temperature density matrix, together with a conventional density-mixing scheme. Calculations were done using both the local density approximation (LDA) [9] and with gradient corrections (GGA) [10, 11] to the LDA. We focussed on a system that is well characterised experimentally: the CO/$p(2 \times 2)$-O/Pt(111) co-adsorption system [12], in which the O atoms are chemisorbed on hollow sites in a $p(2 \times 2)$ structure, and CO adsorbed on top sites (Fig 1.). Our periodic system consisted of 3 layers of Pt atoms (4 atoms per layer), 2 O atoms and one C atom. In all the calculations, the bottom two layers of Pt atoms were held fixed in their equilibrium positions, while the top layer of atoms were allowed to relax. Soft pseudopotentials generated by using a kinetic-energy-filter optimisation scheme were employed, and the electronic orbitals were expanded upto 500eV cutoff [16]. The pseudopotentials accurately reproduced the properties of the isolated systems, including equilibrium lattice constant of Pt, the CO bond length and vibrational frequency, the CO_2 bond lengths and vibrational frequencies. Calculations were done using a Monkhorst-Pack mesh of $2 \times 2 \times 1$ and convergence with respect k-point sampling was checked using a $6 \times 6 \times 1$ mesh. A realistic electronic temperature (800K) in the finite temperature density functional was employed. We searched for the low energy pathway taking us from CO/$p(2 \times 2)$-O/Pt(111) to chemisorbed CO_2 using a constrained minimisation scheme. In this approach, we keep the C-O(a) distance fixed at preselected values, and minimise the total energy with respect to all remaining orthogonal degrees of freedom. In particular this means that the molecules are free to rotate and translate subject to the above constraint, and in addition the surface Pt atoms are allowed to relax. The transition state (TS) is identified by requiring (a) that the ionic forces at the TS vanish, and (b) that the TS is a maximum along the reaction coordinate (i.e. C-O(a) distance) , but a minimum with respect to all remaining degrees of freedom. The resulting pathway gave a smooth passage from the initial to final state, which are shown in a series of snapshots in Fig 2.

We comment that this method of obtaining TS's works only if the constrained coordinate is properly chosen. Otherwise one finds discontinuous trajectories, corresponding to different low energy pathways. We experimented with several constraints in which these problems were encountered, but the final choice of the C-O(a) distance was successful in avoiding such problems, and led to smooth pathway and a genuine transition state.

The initial motion in the reaction path is due to the CO molecule moving towards the bridge site B. As the CO molecule arrives at B, the O(a) atom is displaced a small amount away towards the opposite bridge site B' (Fig. 2c). The next event is pivotal. The CO molecule moves from B onto Pt(1), the *O(a) atom simultaneously breaks its bond with Pt(1) and moves to B'* (Fig.2 e). This is the transition state. In the next few steps the CO molecule and O(a) atom move together to form a bond, in the process of which a second O(a)-Pt bond (Pt(3)) is broken. This process is complete in Fig. 2g. The nascent CO_2 thus formed, however, is in an unfavourable location on the surface, and displaces itself to give finally chemisorbed CO_2, which is a highly bent and stretched molecule asymmetrically bonded with the surface (Fig. 2h), with O(a) bonded to Pt(2) and the C atom to Pt(1).

The chemical bonding changes dramatically in the course of this pathway. The motion of the CO molecule from the initial configuration to B results in the spreading of electron density to the neighbouring Pt(1) atom, while breaking the three fold symmetry of the electron density

surrounding O(a). In fact

the presence of the CO molecule at B severely weakens that O-Pt bond. At the transition state, the O(a)-Pt(1) bond is completely broken, and O(a) is bonded only to Pt(2) and Pt(3), while the CO molecule has become bonded to Pt(1). The formation of the nascent C-O(a) bond occurs at the transition state. The calculated reaction barrier is 1.01 eV in the LDA and 1.05 eV in the GGA (Fig. 3). Both are in good agreement with the barrier of approximately 1 eV deduced from kinetic experiments [3]. We remark that the difference in the energy barrier predicted by the LDA and GGA is found to be very small in the present system. The transition state has a very interesting feature: distance between C and O(a) is remarkably long, 2.1 Å, compared to the bond length (1.16 Å) between C and O in CO_2 molecules. It indicates that the direct repulsion between chemisorbed CO and chemisorbed O atom may not be so important in generating the reaction barrier. To find the physical origin of the reaction barrier, we calculated O chemisorption energies on Pt(111) without CO. We found that O atoms bonded with three Pt atoms on hollow sites (the same as that in the initial state) are approximately 0.6 eV more stable than the structure with O atoms on bridge sites. Furthermore, the barrier to CO diffusion from a top site to a bridge site in the absence of chemisorbed O atoms is very small, whereas it is approximately 0.5 eV in the presence of such O atoms. The reason for this marked increase in energy is the weakening of the O-Pt(1) bond which occurs when the CO molecule is on the bridge site. The competition for forming surface bonds therefore results in a significant indirect repulsion between the CO molecule and the O atom, which generates a long transition state. The key role of the weakening and breaking of an O-Pt bond suggests that the predominant barrier to the reaction is the strength of this bond. Therefore, the barrier should be lower if the O-metal bonds are weakened. A similar feature has been discussed in CO oxidation on Ru [4].

These findings can explain many of the features found experimentally. The chemisorbed CO_2 species is a highly bent and asymmetric structure, with bond lengths substantially longer than in the gas phase molecule. On desorption from the surface the molecule will be in highly excited vibrational states, as is observed experimentally [13]. Modification of the O atom environment, for example, by their adsorption at sites of surface defects or in disordered configurations, may weaken their surface bonds, and should therefore require lower energies for the reaction to proceed. Indeed this is observed experimentally [12], where the CO oxidation reaction occurs at lower temperatures when disorder is introduced in the O atom chemisorption. The paradoxical behaviour of CO oxidation on Cu can similarly be explained. In this case, the reaction does not occur easily if the O atoms are chemisorbed at room temperature but takes place readily if they are chemisorbed at lower temperatures [14]. We suggest the reason for this behaviour is that at room temperatures the chemisorbed O atoms are tightly bonded, being incorporated as Cu-O-Cu chains [15]. The energetic barrier to breaking such Cu-O bonds is highly unfavorable. On the other hand, O atoms chemisorbed at lower temperatures are more weakly bonded to hollow sites of the surface, and in this case the energetic barrier breaking a Cu-O bond is much lower, enabling the CO oxidation reaction to occur at low temperatures.

The observed pathway has the feature of least bond breaking. The initial motion of CO towards the bridge site *B* does not break significantly weaken any chemical bond. At the transition state only one O-Pt bond is broken, and the competition for bonding is limited to only one Pt atom. In alternative pathways, for example, the linear trajectory taking the CO molecule to the O

atom through a hollow site, involves the competition for bonding of the CO molecule with two Pt atoms which are simultaneously bonded to the O atom. This weakens two O-Pt bonds and we explicitly verified that it is much more energetic (in excess of 2eV). It is plausible and in keeping with general physical principles [17] that minimising the competition for bonding with surface atoms and the number of broken surface bonds are general features of reaction pathways in such systems. Such a simple geometric criterion may be a useful guide in identifying possible low energy pathways.

In this study we have identified a transition state and low energy pathway for CO oxidation on Pt(111) in the Langmuir-Hinshelwood mechanism for the first time, and provide microscopic evidence that the predominant barrier for the reaction is the strength of the bond between the O atoms and the surface. We expect that modifications of this may play a crucial role in determining the efficiency of the catalyst. Very recently, an experimental (scanning tunneling microscopy) study of CO oxidation on Pt(111) was published [18], in which it was found that CO oxidation takes place more readily at the boundaries between O islands and CO islands. This finding is consistent with the results presented here since we expect that the O atoms at such boundaries may be displaced from their ideal $p(2 \times 2)$ sites and therefore provide a lower barrier to reaction with CO than interior oxygens.

Current work is in progress in analysing more quantitatively the properties of the reaction pathway and the transition state, using quantum chemical concepts of Mulliken charges and bond orders. These will be presented in a forthcoming paper.

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Figure Captions

Fig. 1 The geometry of the $CO/p(2 \times 2)O/Pt(111)$ configuration. The unit cell in the surface plane is indicated with dotted lines.

Fig. 2. Snapshots of the reaction pathway from the initial state (top left, a) to the final state (bottom right, h). The lattice vectors are indicated in (a). For clarity, the periodic images of the molecules are not shown, and the view is slightly tilted from the vertical. The Pt atoms are the largest spheres, the O atoms are the darkest spheres, and the small grey spheres are the C atoms. The transition state is (e). In (h), the molecular geometry of the CO_2 molecule is: bond-lengths C-O(a)=1.29Å, C-O(b)=1.21Å, bond-angle: 131°. The gas-phase molecule is linear with a bond-length of 1.16 Å.

Fig. 3. The energies of the 8 configurations show in Fig. 2, relative to the lowest energy configuration. Dashed: LDA; Solid: GGA.

Figures

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Figures