HCM Newsletter

Ψ_k Network

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

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Editorial

The **Editorial** is followed by the section **News from the Network.**There we give the latest news on the *Network Conference* in Schwäbisch Gmünd. The final Conference programme and the complete book of abstracts are to be e-mailed as a separate *LaTeX* document. The size of the printed book of abstracts is 124 pages.

In the section **News from the Working Groups** readers will find reports on recent collaborative visits and the Halle Workshop on *Magnetic Nanostructures on Metal and Semiconductor Surfaces–Theory and Experiment.* The report contains abstracts of all papers presented at the Workshop. Straight after the reports there are announcements of available positions and future workshops/courses.

Abstracts follow the announcements.
The last section of the *Newsletter* contains the **Highlight of the Month** article by T. Grabo, E.K.U. Gross and M. Lüders on *"Orbital Functionals in Density Functional Theory: The Optimised Effective Potential Method".*

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

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

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

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

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

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

News from the Network

Since this is the last *Newsletter* before the Conference in Schwäbisch Gmünd (17–21 September, 1996) we would like to use this opportunity and present you with some useful information.

The good news is that the final Conference programme and the book of abstracts, of all contributions to be presented at the Conference, are ready. The *LaTeX* document containing all this information will be distributed electronically, immediately after the present *Newsletter*. To process it *LaTeX2e* is absolutely essential. Due to a large size of the document (124 pages of A4 format), the postscript file will be made available only upon special request. We would not want to overload most of your mailers! The book of abstracts, the programme, and other Conference information, are also available on World Wide Webb at: `http://radix2.mpi-stuttgart.mpg.de`.
Moreover, the printed books of abstracts, with a fancy Conference logo, will be handed over to all participants at the registration desk at the Conference.

Those of you who have not registered to the Conference, but after studying the programme and book of abstracts would like to do so, may still contact the organizers at: `psik@radix2.mpi-stuttgart.mpg.de`. However, any late registration may be a subject to the availability of hotel places.

Below please find some helpful information on how to get to Schwäbisch Gmünd.

From the Stuttgart Airport: Take the train (**S-Bahn**) to the main railway station (Hauptbahnhof). The train station in the Airport is situated in the underground of the arrival building. Follow the signs showing a large **S**. Before boarding the train you have to buy a ticket from an automatic ticket machine at the entrance to the train platform. The price of the ticket for the ride to the 'Hauptbahnhof' is 4.50 DM and you can use either coins or bills (10 DM, 20 DM, a.s.o.). The frequency of trains is at least three per hour from 5:00 until 24:00. The trip takes 14mins. Any of the three trains (**S1, S2, S3**) can be used.

You will arrive at the underground level of the 'Hauptbahnhof'. At the street level, and on the right hand side of the train station (facing the station building in the street outside), you can buy tickets for the train to Schwäbisch Gmünd. Tickets are also available on the train. The price is 14 DM (return ticket 28 DM) for a second class ticket. The tracks are one level above the street level. The track (=Gleis, in German) number from which the train leaves may be found on the timetables in the station. There are two timetable posters: Abfahrt (= departure) and Ankunft (= arrival). There is at least one train per hour from 5:51 until 23:22. The trip takes about 40mins.

A **taxi** from the Stuttgart Airport to Schwäbisch Gmünd costs about 150–170 DM, although one could try to negotiate a fixed price which might then be somewhat lower.

See you all in Schwäbisch Gmünd!

News from the Working Groups

Report on the collaborative visits of C. Katan (University Rennes I - CNRS, FR) to IBM Zürich Research Laboratory

17-28 January and 22 July - 2 August, 1996

These two visits are related to the existing joint project between P.E. Blöchl (IBM Zürich Research Laboratory), C. Katan and C. Koenig (University Rennes I - CNRS). In this project we perform *ab-initio study of the electronic structure of TTF-CA* and more generally the electronic and dynamical properties of molecular charge-transfer compounds [Newsletters 10, 11 and 13]. During these stays we continued the work on TTF-CA and initiated new studies on TTF-2,5Cl_2BQ compounds.

We calculated the electronic properties of TTF-CA and TTF-2,5Cl_2BQ. Our calculated structures for the low-symmetry phase of TTF-CA agree well with experiment. Our calculations predict for the first time the low-symmetry structure of TTF-2,5Cl_2BQ, as no such experimental information is available to date.

Our goal is to derive all parameters responsible for the transition from first principles. Besides the parameters already mentioned in our previous reports, we have now resolved inter-molecular hopping integrals related to the electronic coupling within and accross the molecular stacks. While the strongest interactions are along the stacks and result in mainly one dimensional behavior, we found that the main interactions across the chains are as large to 20 %.

Expenses:
travel (2 times Rennes -Rüschlikon) : 600 ECU
subsistance (2 times 12 days) : 1440 ECU

(C. Katan)

Report on the Workshop
Magnetic Nanostructures on Metal and Semiconductor Surfaces
- Theory and Experiment -

supported in part by the EU HCM Ψ_k-Network on *Ab-initio* (from electronic structure) calculation of complex processes in materials

1 General Information

The workshop was held on May 20,21 in Halle, Germany. The aim of the workshop was to bring together theorists and experimentalists, working in the field of magnetic nanostructures to discuss the state of the art in calculating magnetic properties of free and supported metallic clusters as well as the present status of experimental studies of such nanostructures.

20 colleages from outside of Halle took part in the workshop coming from Germany, France, Greece, Switzerland, and U.S.A. Together with colleagues and students from Halle University and the MPI of Microstructure Physics we had an audience of 40 people. 15 talks were given in the two days. A total time of 40 minutes per talk gave enough time for a detailed information about the subject and for detailed questions as well. 7 talks were devoted to experimental techniques. In the other 8 talks theoretical results were reported.

In a series of theoretical talks (*Jena, Dreyssé, Andriotis, Hergert, Wildberger*) free and supported TM clusters were considered. Ab intio methods (SCF-LCAO-MO, FLAPW, KKR) and semi-empirical methods (TB, TB-MD) are used for the calculations. The main topic of the talks was to understand the relation between the real structure of the clusters and the magnetic properties and the interaction of the substrate with the supported cluster.

In a series of talks (*Kern, Klaua, Farle*) the creation of metallic nanostructures was discussed. In an impressive talk *Kern* showed, how metallic nanostructures of different size and shape can be generated using preferential growth modes on anisotropic surfaces. A different method wa demonstrated by *Klaua*. The formation of Fe wires on vicinal Cu(111) surfaces can achieved using the pronounced decoration effect of Fe at the upper edges of Cu steps.

The gap between the experimental contributions using the STM and the theoretical contributions dealing with electronic and magnetic properties of small supported clusters was partially bridged by *Heintze, Wildberger*. In these talks it was disussed, how ab initio

methods (FLAPW, KKR) can be used for the interpretation of STM images.
No talks about metallic clusters on semiconductor surfaces were given, but in one contribution (*Pehlke*) the equilibrium shape of InAs quantum dots on a GaAs(001) surface was discussed, using a combination of DFT for the calculation of surface energies and finite-element techiques for the calculation of the elastic energy.
Our intention of the workshop was also to discuss the possibilities of direct measurements on magnetic nanostructures. Here new ideas are necessary to develop such experimental techniques and also the develop a theoretical description of such techniques. If one speculates about technical applications of magnetic nanostructures then the question of such nanoparticles on semiconductor surfaces becomes relvant. Therefore we found at the end the we got all a lot of interesting information during the workshop, but we were faced with much more open questions.

We would like to continue with suh aworkshop next year. Everybody, who has some critical remarks or comments to the workshop is invited to contact us. Also proposals for the next time (spring 1997) or interest in participation should be mailed to us.

The workshop was organized in cooperation of the Martin-Luther-University (*W. Hergert*) and the Max-Planck-Institute of Microstructure Physics (*J. Kirschner*). The financial support of the network is greatfully acknowledged again.

(W. Hergert)

2 Abstracts of the talks

- **MO-1**
  EVOLUTON OF MAGNETISM: FROM ATOMS TO BULK
  P. Jena
  Virginia Commonwealth University, Richmond, Virginia, U.S.A.

  The evolution of magnetism as systems grow from atoms to linear chains to monolayers and multilayers illustrates the role of dimensionality on the magnetic moment of both magnetic and nonmagnetic elements. It is well known that low dimensionalty can induce ferromagnetic order. The study of clusters has added a new dimension to this interesting field as clusters are characterised by low dimensions as well as reduced size and symmetry. Thus a comprehensive understanding of how magnetism depends on these factors can not only provide a fundamental understanding of magnetism but may be useful in the design of novel magnetic materials. Results based upon state-of-the -art calculations will be presented that illustrate the role of dimension, size, symmetry and temperature on magnetism of fintite systems.

- **MO-2**

MAGNETIC CONFIGURATIONS OF RHODIUM CLUSTERS

H. Dreyssé[1], J. Dorantes-Dávila[2]

[1] *Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur, 23 rue du Loess, F-67037 Strasbourg, France;* [2] *Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, Mexico*

Two configurations are, *a-priori* favorable for a possible magnetic ground state of Rhodium: very thin films and small clusters . In both cases, the reduction of the average coordination number could allow the onset of magnetism. For thin films of Rhodium on Silver, the Ag/Rh interdiffusion inhibits a long range magnetic order. The only favorable case is to consider a magnetic substrate.

For clusters, experimental works indicate that Rh_N clusters with $N \simeq 60$ have a non-zero average magnetic moment. By using a d-band Hubbard Hamiltonian, the size and the geometric dependence of the magnetic properties of Rh clusters is studied. Different structures and atomic relaxations are considered. Significative magnetic moments are found upto $N \simeq 50$.

- **MO-3**

MAGNETIC PROPERTIES OF CLUSTERS OF TRANSITION METAL ATOMS

A. N. Andriotis[1] N.Lathiotakis(1,2) and M.Menon(3,4)

(1) Institute of Electronic Structure and Laser,Foundation for Research and Technology, P.O.Box 1527, 71110 Heraklion, Greece, (2) Physics Dept. University of Crete, 71409 Heraklion Greece, (3) Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, (4) Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0055

Using a newly proposed calculational scheme that combines the Hubbard approximation with the Tight-Binding Molecular Dynamics method, we calculated the magnetic moments of Fe_n and Ni_n clusters with number of atoms $n \leq 55$. Our results indicate that the average magnetic moment per atom is much higher than the corresponding bulk value in agreement with recent experimental data for Fe and Ni clusters. Furthermore, it is found that magnetic effects stabilize the clusters in geometries that were found completely unstable when magnetism is ignored. In general, magnetic effects drive Fe (and to less extent Ni) clusters to geometries of higher symmetry than that of the corresponding singlet states.

- **MO-4**

METAMAGNETIC STATES OF 3d NANOSTRUCTURES ON THE CU(001) SURFACE

W. Hergert[1], V.S. Stepanyuk[2], P. Rennert[1], K.Wildberger[3], R. Zeller[3], P.H. Dederichs[3]

[1]*Martin-Luther-Universität Halle-Wittenberg, FB Physik, 06099 Halle,* [2]*Max-Planck-Institut für Mikrostrukturphysik Halle, 06120 Halle, Germany,* [3]*IFF, Forschungszentrum Jülich, 52425 Jülich, Germany*

Different magnetic states for a given real structure are known for bulk metals and alloys and also for free transition metal clusters.
We have calculated the magnetic properties of small 3d transition metal clusters on the Cu(001) surface by means of an *ab initio* KKR Green's function method. It is shown that multiple magnetic states exist in these nanostructures. High spin and low spin ferromagnetic states as well as antiferromagnetic states occur.
Ti and Ni trimers are nonmagnetic. The trimers from V to Co show a high spin ferromagnetic, a low spin state and an antiferromangetic state. The low spin state changes its character from ferromagnetic (V,Cr) to antiferromagnetic (Fe,Co). The energy differences between different magnetic states can be small (V,Mn).
The dependence of the magnetic states on cluster size and geometry is also presented.

- **Mo-5**

METAL NANOSTRUCTURES AT SURFACES : GROWTH, FORM AND STABILITY

Klaus Kern
Institut de Physique Expérimentale, EPF Lausanne, CH-1015 Lausanne, Switzerland

Nanofabrication combines physical and chemical processes to assemble structures on the atomic level. Despite the remarkable success of building individual nanostructures of arbitray size and shape with the scanning tunneling microscope, the controlled parallel fabrication of nanostructures is a continuing challenge. Particular promising are techniques in which nanostructures form spontaneously , i.e. self-assemble, guided by the building codes of nature.
In this talk we will focus on the fabrication of nanostructures via self-organized growth. In the kinetic growth regime the hierarchy of activated surface motion can be used to translate random motion into geometrical order. By exploiting the dependence of the mobility of adsorbed atoms on substrate crystal face and temperature, we are able to grow one- and two-dimensional metal nanostructures with a great variety of forms and sizes. The high number density (10*11-10*14 cm*-2) of these structures means that their physical and chemical properties can be easily measured with conventional surface spectroscopies. The underlying kinetic surface processes, like diffusion, nucleation and aggregation are discussed and their implication for selforganized two-dimensional growth is outlined.

- **Mo-6**

FABRICATION OF Fe WIRES ON CU(111) AND THEIR MAGNETIC PROPERTIES

M. Klaua
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The formation of continuous Fe wires on a Cu(111) vicinal surface benefits from the pronounced decoration effect of Fe exclusively at the upper edges of Cu steps. At a deposition temperature of 300K and a coverage range of 0.4 to 1.1 ML Fe quasi one-dimensional Fe stripes along the Cu steps are formed having dimensions of 3-10 nm width and 1-3 ML height at typical step distances of 5-30nm. Nucleation of 2 ML Fe islands on the terraces plays only a minor role. In addition to the wire formation, at 300K also Cu diffusion processes are induced by strain driven mechanisms resulting in the formation of two-dimensional Cu holes in the terraces: The size of holes monotonously grows with the time after deposition. Recipies for avoiding the hole formation were found by using slightly lower deposition temperatures and immediately cooling down to 150K or by sealing the Fe wires by a deposition of 0.2 ML Au. Magnetic properties of submonolayer coverage of Fe on a vicinal Cu(111) and a flat Cu(111) were measured by magneto-optical Kerr-effect (MOKE). Small but distinct hysteresis loops have been measured in polar geometry at low temperatures indicating an out-of-plane magnetization.

- **Mo-7**

SCANNING TUNNELING MICROSCOPY ON THIN OXIDE FILMS

H. Neddermeyer
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Thin oxide films are of great importance as model substrates for adsorption studies and in layered structures. Their structural characterization has not yet reached the state as has been obtained for metallic layers and we have therefore concentrated in the last years on the preparation of thin ordered oxide films and their analysis by scanning tunneling microscopy (STM). The general problem of STM measurements of such films and their structural characterization is that the STM images can normally not be correlated in a simple way with charge densities of the surface which complicates the derivation of atomic models from the measurements. However, more general properties as, for example, the growth behaviour of the oxide films can always be obtained. In the present talk, typical results on such STM measurements will be given. In particular, the growth and structural properties of NiO(111) and NiO(100) are discussed.

- **Mo-8**

WHAT CAN WE LEARN ABOUT MAGNETISM AND ELECTRONIC STRUCTURE FROM STM

S. Heinze[1], S. Blügel[2]

[1] *Zentrum für Mikrostrukturforschung, Universität Hamburg, D-20355 Hamburg* [2] *Institut für Festkörperforschung des Forschungszentrums Jülich, D–52425 Jülich*

In the interpretation of STM images of clean metal surfaces it is almost always assumed that the protrusions represent the metal atoms. This assumption is particularly dangerous for transition-metal surfaces since the directed bonds due to d-orbitals including d-derived surface states may lead to an anticorrugation of the STM image, depending on the bias voltage. Since the d-orbitals of $3d$ transition-metals are also the origin of the magnetism we may expect a large change of the spatial distribution of the d-orbitals subject to the size of the local magnetic moments. This change of the spatial distribution should affect the STM image. A typical counterargument to this line of thought recalls that the d-orbitals are rather localized and cannot be detected by the STM tip typically a few $\AA$ above the surface. In this contribution we address these problems. We calculated the STM-topography for some selected surfaces (i.e. W(110)) and ultrathin films (i.e. Fe/W(110)) on the basis of Bardeen's perturbation approach. The wavefunctions and charge densities are calculated without any adjustable parameter on the basis of the density functional theory in the local density approximation using the FLAPW-method in the film.

- **Mo-9**

AB-INITIO CALCULATIONS FOR 3d IMPURITIES ON Fe(001) AND Ni(001)

K. Wildberger, B. Nonas, R. Zeller, and P.H. Dederichs

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

We present ab-initio calculations for the electronic structure of 3d impurities on Fe and Ni(001) surfaces. The calculations are based on local density functional theory and apply a KKR Green's function method for impurities on surfaces. We consider single 3d impurities as adatoms on hollow sites in the first "vacuum" layer and as substitutional impurities in the surface layer. For Fe, Mn, and Cr impuritites the moments are considerably enhanced compared to the bulk, but there is surprisingly little difference between the adatom and surface sites. While a Mn adatom couples ferromagnetically to the bulk moments, we find antiferromagnetic coupling for the surface position. The energetics for integrating an adatom into the surface layer and for diffusing into the bulk are discussed. We also perform calculations for adatom dimers and determine their interaction and magnetic coupling.

On the Ni(001) surface the 3d moments are more strongly enhanced than on the Fe surface and within the 3d series a broad two state region exists.

- **Di-1**

MAGNETISM OF IRON AND COBALT ISLANDS ON W(110)

J. Bansmann, L.Lu, M.Getzlaff[1], and K.H. Meiwes Broer
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Magnetic thin films and island structures are an attractive topic, because the magnetic properties sometimes differ from their bulk behaviour. The fundamental physics of magnetism of deposited clusters on surfaces is only scarcely understood. The structure of iron and cobalt on the tungsten (110) surface depends strongly on the temperature of the substrate. In our case the adsorbate systems have been prepared in-situ by thermal evaporation at room temperature onto the clean and annealed W(110) crystal. The thin films have then been heated to a temperature of about 700°C where a phase transition from thin films to island structures occurs. The adsorbate structures are characterized with LEED and photoemission. Additionally a Co-island structure has been examined ex-situ using AFM and STM techniques.
In this contribution we report on measurements with *magnetic circular and linear dichroism in photoemission (MCD/MLD)* at thin Fe and Co films and island structures. The experiments have been carried out in the soft X-ray region at the *SX700/3*-monochromator at the storage ring BESSY in Berlin. For MCD and MLD in photoemission the intensities of the Fe and Co 3p- corel levels and the 3d valence bands depend on the magnetization of the samples. Typical MCD- and MLD-asymmetries of thin films reach values of about 5%. We compare our results for Fe- and Co-island structures to data for epitaxially grown films on W(110).

- **Di-2**

HIGH COERCITIVITY FOR SESQUILAYERS OF Fe ON W(110)

D. Sander, R. Skomski, A. Enders, and J. Kirschner
Max-Planck-Institut für Mikrostrukturphysik, Winbeergweg 2, 01620 Halle

Elastic and magnetic properties of ultrathin iron films on tungsten(110) are investigated. In situ film stress measurements during growth show stress values as high as 25 GPa per deposited monolayer. Our experiments show, how the tremendous film stress triggers the formation of a misfit dislocation net- work already at a coverage of 1.5 monolayers. In situ magneto-optical Kerr-effect measurements reveal a a maximum of the coercivity as a function of the film thickness for a sesquilayer film at a coverage around 1.5 monlayers. A coercivity of 0.3 T is observed, which is almost a factor of ten higher than the coercivities of films with slightly lower or higher coverages. A model is presented that explains the high coercivity in terms of strong domain wall pinning. The influence of an inhomogenous stress-field on the coercivity is discussed.

- **Di-3**

MICROMAGNETIC STRUCTURE AT THE REORIENTATION TRANSITION IN Co/Au(111)

H.P. Oepen
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle

The micromagnetic structure in Co monolayers grown on Au(111) has been investigated by means of the Scanning Electron Microscope with Polarization Analysis (SEMPA). In the low thickness regime hcp Co films have an easy axis of magnetization perpendicular to the film plane due to the predominant surface anisotropy. At higher thicknesses the magnetization turns into the film plane, caused by the magneto-static energy contribution. The thickness where the flip of magnetization occurs is called the magnetic reorientation transition. We have studied in detail the growth of the films and find a strong correlation between film morphology and magnetic domain structure in the as-grown films. The observed domain pattern is similar to that published by Allenspach et al. /1/. By heat treatment the film quality can be considerably improved which causes strong changes of the domain pattern. The micromagnetic structure in the annealed films exhibits characteristic features which are close to the magnetic equilibrium configuration. The comparison with theoretical models based on a stripe domain structure /2/ shows a good agreement. From the fit the surface anisotropy constant can be determined. Magnetizing the films transforms the domain structure into a single domain configuration, which was also reported previously /3/. The single domain state is a meta-stable configuration which can be re-transformed in the multi-domain state by heat treatment, only. Increasing the film thickness causes the magnetization to flip from vertical to in-plane orientation. We studied this magnetic reorientation transition for the single and multi-domain configuration. We do not find any indication for a continuos magnetization rotation via a magnetization canting nor indications for loss of long range order. The results are completely understandable if higher order surface anisotropy contributions are taken into consideration. Based on a new model /4/ the findings can be completely interpreted.

/1/ R. Allenspach, M. Stampanoni and A. Bischof; Phys. Rev. Lett. 65 (1990), 3344

/2/ Z. Malek and V. Kambersky; Czech. J. Phys. 21 (1958), 416

/3/ J. Pommier, P. Meyer, G. Penissard, J. Ferre, P. Bruno and D. Renard; Phys. Rev. Lett. 65 (1990), 2054

/4/ Y. Millev and J. Kirschner; Phys. Rev. B accepted

- **Di-4**

THEORY OF NONLINEAR MAGNETO-OPTICS AND MAGNETIC ANISOTROPY IN METALLIC NANOSTRUCTURES

W. Hübner, J. P. Dewitz, A. Dähn, R. Družinić, and K. H. Bennemann
Institute for Theoretical Physics, Freie Universität Berlin, Germany

The physics of metallic nanostructures is a rising and promising field both of theoretical as well as experimental and applicational interest. Recent (and yet unpublished) results on several aspects of nanostructure theory will be presented.

(i) *Classical Mie theory* is extended to nonlinear optics: Using classical electrodynamics we determine the angular dependence of the light intensities radiated in second and third harmonic generation by spherical metal clusters. The complete angular scattering profile in nonlinear optics, in particular the ratio of forward and backward scattering, is analyzed in detail. It turns out that nonlinear optics, the yield of which is drastically enhanced in clusters compared to flat surfaces due to the curvature, is much more sensitive to the cluster size and shape than linear optics and therefore may become a competitive probe for the investigation of deposited microclusters. Due to the different symmetries of frequency doubling and tripling we find characteristic differences in the angular profile of second and third harmonic. Strong magnetic effects are predicted even in the Rayleigh limit.

(ii) We study the *nonlinear magneto-optical Kerr effect* of vertically and laterally nanostructured thin magnetic films. Using an electronic theory we find strong quantum well oscillations for Cu/Fe (001) multilayer systems. Their amplitude is enhanced by several orders of magnitude compared to linear optics due to an additional degree of freedom in nonlinear magneto-optics. Two oscillation periods are found in our theory. On lateral nanostructures, in particular of triangular symmetry, we expect that nonlinear magneto-optics can characterize structures that are not visible in linear optics due to the local field enhancement and the symmetry of three-photon mixing. A complete group-theoretical analysis shows how the interplay of structure and magnetism allows for the imaging of ferromagnetic and antiferromagnetic domains in nanostructured films using the nonlinear Kerr effect.

(iii) We present a tight binding calculation for the *magnetocrystalline anisotropy energy of finite one-dimensional magnetic nanostructures* such as dimers, chains (quantum wires), or rings (quantum corrals) as a function of atom number, magnetic configuration, and electronic occupation. In particular, we find the following results: The anisotropy decreases with increasing system size for both rings and corrals. As expected, the dimer anisotropy energy E_{anis} (per atom) is much larger than in thin films (16 meV) due to the reduced symmetry. However, for increasing system size, it gradually approaches the monolayer values (0.8 meV for the 48-corral). The rings of N Fe atoms (N=3...48) exhibit odd-even oscillations of the anisotropy which are absent in the linear configurations. The energy-level scheme and thus the magnetic anisotropy energy is asymmetric with respect to half filling of the d states if the bonding is mixed of π and δ character. A generalization of Hund's third rule is proposed.

- **Di-5**

NANOSTRUCTURING OF THE Cu(001) SURFACE BY ION BOMBARDMENT : A STM STUDY

M. Farle, M. Ritter, M. Stindtmann, and K. Baberschke
Institut für Experimentalphysik,Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

A detailed investigation of the effects of ion bombardment and thermal treatment on the topography of Cu(001) surfaces is presented. By means of 400 eV Ar+ bombardment (flux $6 \cdot 10^{12}$ ions cm^{-2} $\sec^{-1}$) at 300 K rectangularly shaped vacancy islands are created. These wells are on average 5 atomic layers deep, typically 20 nm wide at the top and regularly spaced about 27 nm apart. The dependence of this periodic well structure on the ion beam parameters and thermal treatment is discussed. Annealing the crystal to 370 K completely flattens this structure and the smooth topography of the clean unbombarded Cu (001) surface is recovered. This technique may offer a new cost efficient approach to produce large scale magnetic nanostructures from thin films.

- **Di-6**

THE EQUILIBRIUM SHAPE OF InAs QUANTUM DOTS GROWN ON A GaAs (001) SUBSTRATE

E. Pehlke, N. Moll, A. Kley, and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem

During the heteroepitaxy of InAs on a GaAs (100) substrate small three-dimensional islands form. This is due to the energy gain by elastic relaxation of the islands, which over-compensates the energy cost due to the increase in surface energy. The role of energetic and kinetic effects determining the shape and size of these islands have been discussed controversially.[1,2]

In this talk I will concentrate on the energetic aspect and present our theoretical approach to predict the equilibrium shape of the InAs quantum dots as a function of their size.

We have calculated the surface energies for various surface reconstructions of the (110), (100), (111), and $(\bar{1}\bar{1}\bar{1})$ surfaces of InAs using density-functional theory and the energy-density formalism by Chetty and Martin.[3] A finite-element approach is used to compute the elastic energy of the strained, dislocation-free (i.e., coherent) InAs islands within continuum theory. To investigate the equilibrium shape of the strained islands we combine these two results and identify the energetically favored

shape.

1) C. Priester and M. Lannoo, Phys. Rev. Lett. **75**, 93 (1995).

2) V. A. Shchukin, N. N. Ledentsov, P. S. Kope'ev, and D. Bimberg, Phys. Rev. Lett. **75**, 2968 (1995).

3) N. Chetty and R. Martin, Phys. Rev. B **45**, 6074 (1992).

Announcement

Ph. D. Position

Inst. für Phys. Chemie, University of Munich, Germany

There is a Ph. D. position available within the project on *"Ab–initio investigations on the spinodal ordering and segregation of the alloy system Cu-Zn-Al"* funded by the 'Deutsche Forschungsgemeinschaft'.

Starting date: Now
Duration: 2 years + 1 year (presumably)
Salary: BAT 2a/2 i.e. around 1700 DM after tax
Where: Inst. für Phys. Chemie, University of Munich
Requirement: Experience in computational solid state phyics (the more the better)
Techniques used: KKR-CPA, LAPW, MD

Contact and further information:

Prof. Dr. H. Ebert
Institut für Physikalische Chemie
Universität München
Theresienstr. 37-41
D-80333 München

Tel.: (089) 23 94 - 46 42 / - 42 18
Fax.: (089) 28 05 - 248 and (089) 23 94 - 4158
Email: he@gaia.phys.chemie.uni-muenchen.de

Announcement

Post–doctoral Position

Theoretical Physics

H.H. Wills Physics Laboratory, University of Bristol, U.K.

Applications are invited from European Union nationals, excluding U.K. residents, for the above post funded by a European Training and Mobility Award. The award itself is for four years but appointment to the post may be for any part of it starting from 1 October 1996. The successful applicant would be expected to work on the **theory of oscillatory magnetic coupling in metallic multilayers with alloy spacers**, under the supervision of Professor B.L. Gyorffy. There will be opportunities to collaborate with our partners in the grant from Vienna, Strasbourg, Eindhoven, Jülich, and Daresbury. Some experience in electronic structure calculations is essential. The salary will be on the Research Assistant scale, starting from 15,000 GBP per annum. Interested candidates should contact Professor Gyorffy for further information and send a C.V. with names of two referees.

Closing date 1 October 1996.

Professor B.L. Gyorffy
H.H. Wills Physics Laboratory
University of Bristol
Tyndall Avenue
Bristol, BS8 1TL, U.K.
tel.: +44-117-928 8704
fax: +44-117-925 5624
email: blg@siva.bris.ac.uk

Announcement

Post–doctoral Position

Magnetic Multilayers

Daresbury Laboratory, U.K.

Applications are invited from European Union nationals, excluding U.K. residents, for the above post funded by a European Training and Mobility Award. The award itself is for four years but appointment to the post may be for any part of it starting from 1 October 1996. The successful applicant would be expected to work on the **theory of photoemission of magnetic multilayers**, under the supervision of Professor W.M. Temmerman. There will be opportunities to collaborate with our partners in the grant from Vienna, Strasbourg, Eindhoven, Jülich, and Bristol. Some experience in electronic structure calculations is essential. The salary will be on the Research Assistant scale, starting from 15,000 GBP per annum. Interested candidates should contact Professor Temmerman for further information and send a C.V. with names of two referees.

Closing date 1 October 1996.

Professor W.M. Temmerman
CCLRC Daresbury Laboratory
Warrington, WA4 4AD, Cheshire, U.K.
tel.: +44-1925-603 227
fax: +44-1925-603 634
email: w.m.temmerman@dl.ac.uk

Announcement

Post–doctoral Positions

Physics Department, Keele University, U.K.

Professor Mike Gillan has two postdoctoral positions available immediately to work on the first-principles simulation of condensed matter. The projects are concerned with the simulation of molecular processes at oxide surfaces, and with the simulation of liquid metals. Appointment to these posts will be made for one year in the first instance, with the possibility of extension for a further period.

The Keele group has played a prominent role in first-principles simulation over the past seven years, and is currently very active both in surface-science and liquid-state research. We have also recently proposed new techniques in order-N (linear-scaling) first-principles simulation. Mike Gillan is coordinator of the U.K. Car-Parrinello consortium, a collaboration of 10 U.K. research groups which has pioneered the application of massively parallel computing to first-principles simulation. Through this consortium, the Keele group has access to the 512-processor Cray T3D supercomputer at Edinburgh Parallel Computer Centre. Web pages of the Keele Research group and the UKCP consortium are at URL:

`http://www.keele.ac.uk/depts/ph/tc/cph_hme.html`
`http://www.dl.ac.uk/TCSC/projects/UKCP/ukcp.html`

Applicants for the two post-doctoral positions must have an outstanding background in computational condensed-matter physics, chemistry or materials science. A strong track record in first-principles simulation or electronic structure theory, and proven abilities in large-scale code development are also essential for these positions. Applicants must have a Ph.D. in a relevant research area, or expect to obtain one in the next few months.

If you think you might be suitable for either of these positions, please send a mail with your c.v. to Mike Gillan at **pha71@keele.ac.uk**.

Professor Mike Gillan
Physics Department, Keele University
Keele, Staffordshire ST5 5BG, U.K.
Telephone: (+44) 1782-583339
Secretary: (+44) 1782-583326
Fax: (+44) 1782-711093
World Wide Web: `http://www.keele.ac.uk/depts/ph/tc/cph_hme.html`

Announcement

Positions in MSI

MOLECULAR SIMULATIONS

(First appeared in the 20 Jul 1996 issue of New Scientist)

We are the leading provider of software and services for computer-aided molecular and materials science wih revenues of over 50 million US dollars. Our computational chemistry software is used by the world's foremost R&D facilities to predict and explain the properties of chemical systems, improving the development and design of an enormous variety of products and processes.

We are now undertaking a significant expansion of our European Operation, headquartered in Cambridge, UK. We seek several outstanding individuals to join our multi-disciplinary, multi-national European team which features high calibre scientists with backgrounds in biochemistry, chemistry, crystallography, computing, materials science, mathematics and physics. Six positions are based in Cambridge and one in Munich.

PRODUCT MARKETING AND APPLICATION SCIENCE

Product Marketing - Crystallization

You will support our software and services for crystallization research in conjunction with our Product Manager, Crystallization. This will involve extensive liaison with customers, internal sales and R&D organisations as well as external scientific advisors and consultants. You will also participate in fundamental and applied research and present at international conferences.

You will have a PhD in chemistry, pharmacy or physics, a proven track record of applying molecular modelling techniques to crystallization problems as well as an appreciation of the full potential for development of crystallization products. You must be prepared for frequent international travel.

Applications Scientists - Material Sciences

Quantum Mechanics Specialist - Munich Polymer Modelling Expert - Cambridge

You will support our complete range of material science products by advising customers on the application of our software to ther research problems as well as scientifically validating new software developments. You will also present the findings of software related scientific work to conferences, and give on-site technical presentations and demonstrations to potential customers in support of sales. For the Munich position, you will have practical experience of ab initio quantum mechanics; the Cambridge opportunitydemands expert knowledge of polymer and mesoscale modelling. For both positions, you will need a PhD in chemistry or a related area.

PRODUCT DEVELOPMENT

Scientist - Analytical Instruments

We have a major initiative to develop an market a complete suit of simulation products for diffraction, microscopy and spectroscopy. Your role will be to expand and improve this suite and make it available to a broader range of users via the World Wide Web. You will have the opportunity to pioneer the use of web technologies such as Java for chemical computing applications.

Ideally, you will have a degree and PhD in a scientific subject, experience of analytical instruments and C, C++ and FORTRAN.

Scientist - Quantum Mechanics

You will be responsible for the evolution and progression of our Cerius 2IM Quantum Mechanics Workbench. Launched last year, this is already used by hundreds of industrial and academic researchers to understand and design molecular structure and chemical reactions. You will have a PhD, extensive knowledge of the theory and practical application of quantum mechanical methods in chemistry and solid state physics, and a proven record in FORTRAN programming. Experience of packages such as CASTEP, Gaussian, MOPAC, ADF, Turbomole, ZINDO and DMol would be an advantage.

Principal Scientist and Scientist - Simulation Methods

As part of the team which develops DiscoverTM and Open force FieldTM, the premier software for force field based simulation methods, you will be at the leading edge of classical simulations for life and materials sciences in a period of aggressive technology integration and scientific development.

You will have a PhD in chemistry or physics, excellent C/FORTRAN skills and good knowledge of classical force field techniques and applications.

EUROPEAN CUSTOMER SERVICE AND TRAINING

Post-Sales Support Scientist - Material Sciences

Scientist - Quantum Mechanics

You will be responsible for the evolution and progression of our Cerius 2IM Quantum

Mechanics Workbench. Launched last year, this is already used by hundreds of industrial and academic researchers to understand and design molecular structure and chemical reactions. You will have a PhD, extensive knowledge of the theory and practical application of quantum mechanical methods in chemistry and solid state physics, and a proven record in FORTRAN programming. Experience of packages such as CASTEP, Gaussian, MOPAC, ADF, Turbomole, ZINDO and DMol would be an advantage.

Principal Scientist and Scientist - Simulation Methods

As part of the team which develops DiscoverTM and Open force FieldTM, the premier software for force field based simulation methods, you will be at the leading edge of classical simulations for life and materials sciences in a period of aggressive technology integration and scientific development.

You will have a PhD in chemistry or physics, excellent C/FORTRAN skills and good knowledge of classical force field techniques and applications.

EUROPEAN CUSTOMER SERVICE AND TRAINING

Post-Sales Support Scientist - Material Sciences

Your key role will be to support the complete range of our Insight IITM material science products. This will involve providing high level scientific advice and training to our customers. You will help with software installation and maintenance and the application of software to users' research problems, which may involve on-site visits.

You will have a PhD in chemistry or physics and, ideally, at least two years' postdoctoral experience of computer modelling in materials science. In-depth knowledge of our products (including Life Sciences), particularly Insight IITM and DiscoverTM, fluency in French or German and experience of international customer services would all be distinct advantages.

These roles offer the chance to make a significant contribution to an organisation which is consistently at the forefront of technological development. In return, we offer excellent remuneration packages and relocation assistance. Please send a CV, including salary details, to: **Karen Harbach, Administration Manager, Molecular Simulations, 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE. Email kharbach@msicam.co.uk. Tel: +44 1223 413300. Fax: +44 1223 413301.** WWW: `http://www.msi.com}`.

Please mention New Scientist Planet Science when responding to this advertisement.

Announcement

EXCAM Workshop in Paris

26–28 September, 1996

The 1996 EXCAM Workshop (Electronic exchange and correlation in advanced materials) will be held at the Ecole Polytechnique, Paris, from the morning of Thursday 26 September to the evening of Saturday 28 September.

Full details of the workshop, including an application form, are now available on the Web at **http://www.york.ac.uk/ rwg3/excam.html**.

The deadline for applications is 15 August, with an earlier deadline of 22 July for anyone wishing to apply for a bursary or who desires accommodation in the Ecole. Accommodation will be assigned on a first-come-first-served basis.

Rex Godby
Department of Physics
University of York
Tel.: (+44) (0)1904 432231
Fax : (+44) (0)1904 432214
E-mail: rwg3@york.ac.uk

Announcement

Second ψ_k Computer Course on Molecular Dynamics

(Berlin, November 4 - 9, 1996)

Ab-initio molecular-dynamics calculations of structural, elastic, and vibrational properties of poly-atomic systems

In this course the basic concepts of density-functional theory calculations will be explained, and an introduction to the computer program **fhi96md** will be given. This program allows calculations for molecules, perfect crystals, defects in crystals, and crystal surfaces for materials as different as semiconductors, simple and transition metals, insulators, etc. Although it is feasable to treat systems with a few hundred atoms, the hardware needs are just a 12 k ECU workstation and it runs even on inexpensive PENTIUM PC's.

The course will start on Monday afternoon 3 pm, November 4, and will end on Saturday morning, November 9, 1996. Every morning there will be lectures on density-functional theory, the local-density approximation for the exchange-correlation energy-functional, the generalized gradient approximation, the ab-initio pseudopotential approach, molecular dynamics, etc. The afternoon is devoted to hands-on training with computations of simple physical properties, using the computer code **fhi96md**. Examples of these calculations may include:

- bonding and vibrational properties of simple molecules (e.g. Si_2, C_2, and CO)
- lattice constant, bulk modulus, and phonons of Si and GaAs.
- structural phase transitions (Si, diamond $\leftrightarrow$ β-tin structure)

PhD students and postdocs who are interested in attending this course should send their applications to

Dr. José Luís Martins
e-mail: Jose.L.Martins@inesc.pt
fax: +351-1-314 58 43

The letter should include a short (1 page) description of a scientific project which the applicant plans to study subsequently to the course.

The course will take place at the Fritz-Haber-Institut of the Max-Planck-Gesellschaft in Berlin (Germany). Lodging has been reserved in Dahlem Guesthouse (400,- DM per week incl. breakfast). Participants belonging to the Human Capital and Mobility Network "Ab initio (from electronic structure) calculation of complex processes in materials" can receive upon request financial support for the local as well as for the travel expenses. This request should be signed by the node manager. A *limited* financial support is also available for other participants.

Applications should be sent no later than July 15 by e-mail or fax to Dr. J. L. Martins. The number of participants will be limited to 20 persons. Information about acceptance or non-acceptance will be sent out by late July.

Applicants are expected to have a profound knowledge of quantum mechanics and the physics and chemistry of bonding. Furthermore a good knowledge of FORTRAN and UNIX is required. All this should be stated clearly in the application. The course will be organized by Drs. J. L. Martins, J. Neugebauer, and M. Scheffler. together with significant support from the Theory Department of the Fritz-Haber-Institut.

Some ideas about the computer code and its applicability can be found in the following references:

1. R. Stumpf and M. Scheffler: "Simultaneous calculation of the equilibrium atomic structure and its electronic ground state using density-functional theory", Comp. Phys. Commun. **79**, 447 (1994).
2. J. Neugebauer and M. Scheffler: "Adsorbate-substrate and adsorbate-adsorbate interaction of Na and K adlayers on Al (111)", Phys. Rev B **46**, 16067 (1992).
3. R. Stumpf and M. Scheffler: "Theory of self-diffusion at and growth of Al (111)", Phys. Rev. Lett. **72**, 254 (1994).
4. J. Neugebauer and C. G. Van de Walle: "Hydrogen in GaN: Novel Aspects of a Common Impurity", Phys. Rev. Lett., **75**, 4452 (1995).
5. E. Pehlke and M. Scheffler: "Hydrogen adsorption and desorption from Si (001)", Phys. Rev. Lett. **74**, 952 (1995).
6. B. Hammer and M. Scheffler: "Local chemical reactivity of a metal alloy surface", Phys. Rev. Lett. **74**, 3487 (1995).
7. C. Stampfl and M. Scheffler: "Anomalous behavior of Ru for catalytic oxidation: A theoretical study of the catalytic reaction $CO + 1/2\ O_2 \longrightarrow CO_2$, submitted to Phys. Rev. Lett.

Up-to-date information together with the computer code, references and examples may be obtained from the world-wide-web server:

http://www.fhi-berlin.mpg.de/th/fhi96md.html

Ab-initio calculations of the interlayer exchange coupling of Fe-/Co-/Ni-layers in Cu(100)

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

Abstract

Ab-initio calculations for fcc Fe, Co and Ni layers in Cu(100) have been performed using a KKR Green's function method for planar defects. The exchange coupling energy of magnetic bilayers was calculated from the single particle energies within the framework of the frozen potential approximation. The calculations revealed that for Ni the amplitude of the long and the short period is strongly reduced compared with Co and Fe. While the short period dominates the coupling for Ni and Co layers, the long period becomes important in the case of Fe. The asymptotic behavior for large spacer thicknesses and the amplitudes of the different oscillation periods are discussed with the help of spin- and $\mathbf{q}_{||}$-resolved density of states and the corresponding bulk bandstructures of the magnetic layers. For the longer period the minority bands of Ni are sp-like and very similar to the Cu bands, while the corresponding Co bands contain a larger d-admixture. In contrast to this, in the case of Fe the Fermi level is situated in a band gap slightly below the Δ_1-band.

(submitted to J. Magn. Magn. Mat.)

Manuscripts available from: wildberg@iff194.iff.kfa-juelich.de

Ab-initio calculations for 3d impurities on Fe(001) and Ni(001)

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

Abstract

We present ab-initio calculations for the electronic structure of 3d impurities on Fe and Ni(001) surfaces. The calculations are based on local density functional theory and apply a KKR Green's function method for impurities on surfaces. We consider single 3d impurities as adatoms on hollow sites in the first "vacuum" layer and as substitutional impurities in the surface layer. For Fe, Mn, and Cr impurities the moments are considerably enhanced compared to the bulk, but the moments of the adatom and the surface site differ surprisingly little in size. While a Mn adatom couples ferromagnetically to the bulk moments, we find antiferromagnetic coupling for the surface position. We also perform calculations for adatom dimers and determine their magnetic coupling. On the Ni(001) surface the 3d moments are more strongly enhanced than on the Fe surface and within the 3d series a broad two state region exists.

(submitted to J. Magn. Magn. Mat.)

Manuscripts available from: wildberg@iff194.iff.kfa-juelich.de

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

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[†] *Department of Physics, University of Warwick, Coventry, U.K.*
[‡] *Department of Physics, University of Monash, Australia*
[§] *Computational Materials Science Department,*
Sandia National Laboratories, Livermore, CA, U.S.A.

Abstract

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

(submitted to J. Phys. Condens. Matter)

Manuscripts available from: phrjz@weedy.warwick.ac.uk

Photoemission theory for strongly correlated systems

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D-10115 Berlin, Germany
[2] *Fachbereich Physik, Universität Osnabrück,*
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Abstract

A theory of valence-band photoemission and inverse photoemission from single-crystal surfaces is proposed that allows for an inclusion of electron-correlation effects beyond the local-density approximation of density-functional theory. It represents a proper modification and generalization of the famous one-step model of Pendry and co-workers. In a first step we set up and discuss a unified framework for combining standard ab-initio band-structure calculations with many-body methods to derive the one-electron Green function. Starting from first principles, the basic theory of photoemission and inverse photoemission spectroscopy is developed in a second step. It shows the (fully interacting) Green function to determine the bare spectra. Finally, line-shape modifications and dipole selection rules have to be taken into account by correcting the bare spectra for the energy- and wave-vector dependence of the transition-matrix elements. For this purpose we apply the layer-Korringa-Kohn-Rostocker technique and the linear-muffin-tin-orbitals method. Is is demonstrated that by this means a computational implementation is possible that is highly efficient. The theory will be applicable especially for a quantitative analysis of (inverse) photoemission spectra from materials in which the electronic structure is considerably affected by strong electron correlations. Such correlation effects will correct peak positions and may give rise to satellite features and quasi-particle damping. The theory is intended to facilitate the understanding of the combined influence of band-structure, electron-correlation, matrix-element and surface effects on the spectra.

(submitted to Phys. Rev. B)
Manuscripts available from: JBRAUN@dosuni1.rz.Uni-Osnabrueck.DE

Shallow Thermal Donor Defects in Silicon

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Luleå, S95187, Sweden
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Department of Atomic Physics, Technical University of Budapest,
Budafoki út 8, H-1111 Budapest, Hungary

Abstract

An *ab initio* local density functional cluster program, AIMPRO, is used to examine nitrogen related shallow thermal donor defects in silicon. We find the bonding of oxygen with interstitial nitrogen in N_i-O_{2i} to be almost 'normal' but the O atoms move slightly out of their bond centered sites causing the deep donor level of N_i to become shallow. The defect has properties consistent with those experimentally observed for shallow thermal donors. We also find that a C_iH-O_{2i} defect has very similar electronic properties, and suggest that shallow thermal donors do not have a unique composition.

(To be published in Physical Review Letters, 22nd July 1996)

Pre-prints / any communication to Chris Ewels, ewels@excc.ex.ac.uk

Point-charge electrostatics in disordered alloys

C. Wolverton, Alex Zunger, S. Froyen, and S.-H. Wei
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Abstract

A simple analytic model of point-ion electrostatics has been previously proposed [R. Magri, S. -H. Wei, and A. Zunger, Phys. Rev. B **42**, 11388 (1990)] in which the magnitude of the net charge q_i on each atom in an ordered or random alloy depends linearly on the number $N_i^{(1)}$ of unlike neighbors in its first coordination shell. Point charges extracted from recent [J. S. Faulkner, Y. Wang, and G. M. Stocks Phys. Rev. B **52**, 17106 (1995)] large supercell (256-432 atom) local density approximation (LDA) calculations of $\mathrm{Cu}_{1-x}\mathrm{Zn}_x$ random alloys now enable an assessment of the physical validity and accuracy of the simple model. We find that this model accurately describes (i) the trends in q_i *vs.* $N_i^{(1)}$, particularly for fcc alloys, (ii) the magnitudes of total electrostatic energies in random alloys, (iii) the relationships between constant-occupation-averaged charges $\langle q_i \rangle$ and Coulomb shifts $\langle V_i \rangle$ (i.e., the average over all sites occupied by either A or B atoms) in the random alloy, and (iv) the linear relation between the site charge q_i and the constant-charge-averaged Coulomb shift $\overline{V}_i$ (i.e., the average over all sites with the same charge) for fcc alloys. However, for bcc alloys the *fluctuations* predicted by the model in the q_i *vs* V_i relation exceed those found in the LDA supercell calculations. We find that (a) the fluctuations present in the model have a vanishing contribution to the electrostatic energy. (b) Generalizing the model to include a dependence of the charge on the atoms in the first *three (two) shells* in bcc (fcc) - rather than the first shell only - removes the fluctuations, in complete agreement with the LDA data. We also demonstrate an efficient way to extract charge transfer parameters of the generalized model from LDA calculations on small unit cells.

(Phys. Rev. B (in press - Sept. 15))
Preprints available at **http://www.sst.nrel.gov/preprints/preprints.html**

Adlayer core-level shifts of random metal overlayers on transition-metal substrates

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[b] *Max Planck Institut für Physik komplexer Systeme, Außenstelle Stuttgart,*
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CZ-180 40 Prague 8, Czech Republic,
[e]*Institute of Technical Electrochemistry, Technical University,*
A-1060 Vienna, Austria

Abstract

We calculate the difference of the ionization energies of a core-electron of a surface alloy, i.e., a B-atom at the A_xB_{1-x} overlayer on an fcc-B(001)-substrate, and a core-electron of the clean fcc-B(001) surface using density-functional-theory. We analyze the initial-state contributions and the screening effects induced by the core hole, and study the influence of the alloy composition. Data are presented for Cu_xPd_{1-x}/Pd(001), Ag_xPd_{1-x}/Pd(001), Pd_xCu_{1-x}/Cu(001), and Pd_xAg_{1-x}/Ag(001), changing x from 0 to 100 %. It is shown that screening effects can be very important rendering the standard analysis of adlayer core-level shifts an (in general) unreliable tool for analyzing trends in chemical reactivity. However, if used in combination with state-of-the-art theory significant information can be obtained.

(submitted to Phys. Rev. Lett.)
Manuscript available from: vero@fysik.dtu.dk

Experimental and theoretical study of the electronic structure of Fe,Co and Ni aluminides with the *B2* structure

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[1]*Dept of Materials Science and Metallurgy, Univ. of Cambridge,*
Pembroke St, Cambridge, CB2 3QZ, U.K.
[2]*Daresbury Laboratory, Warrington, WA4 4AD, U.K.*

Abstract

The differences in electronic structure of B2-type (CsCl) transition-metal aluminides (FeAl, CoAl and NiAl) have been investigated by comparing data obtained using electron energy-loss spectroscopy with theoretical calculations of the spectra. The densities of states (DOS) for the three alloys calculated using ab-initio self-consistent linear muffin-tin orbital method within the local density approximation have been compared. Using the unoccupied part of the DOS and the relevant transition matrix elements, energy-loss spectra have been calculated. It is noted that a rigid band model can only be used as a first approximation to calculate the trends in the electronic structure of the alloys. The Al L23 and K edges (providing information on s+d symmetry of final states at the Al sites, respectively) and the transition-metal L23 edges (s+d symmetry of final states at the transition metal sites) have been studied. Good agreement has been found between experiments and calculations and, from the interpretation of spectral details in terms of site and angular momentum decomposed density of states, hybridization between the Al sp and TM d bands is observed and thus a covalent character in the bond is concluded. The differences in the electronic structure of the alloys studied, both in terms of the band filling and density of states at the Fermi level, have been correlated with the variation of the macroscopic properties of the materials.

(Physical Review B, 15 July 1996)
available from: Gianluigi Botton, e-mail: gb10003@cus.cam.ac.uk

Towards a Potential-based Conjugate Gradient Algorithm for order-N Self-Consistent Total Energy Calculations

Xavier Gonze

Unité de Physico-Chimie et de Physique des Matériaux,

Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

Abstract

The determination of the total energy within Density Functional Theory can be formulated as a minimisation problem in the space of trial self-consistent potentials. In order to apply a conjugate-gradient algorithm to this problem, a new formula for the computation of the gradient of the energy with respect to the self-consistent potential is proposed. The second derivative of the energy with respect to potential changes is also analyzed, in order to obtain an efficient preconditioning operator. The wavefunctions do not appear explicitely in this approach, so that order-N algorithms could take advantage of it. The results of preliminary tests are reported.

(to be published in Phys. Rev. B, August 15, 1996, as a brief report)

Preprints available from: gonze@pcpm.ucl.ac.be

Electronic Structure of the 1 × 1 $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ Superlattice: A local-spin-density approximation with on-site Coulomb interaction

M. Biagini, C. Calandra, and Stefano Ossicini
Istituto Nazionale per la Fisica della Materia
and Dip. di Fisica, Università di Modena,
via Campi 213/A, I-41100 Modena, Italy

Abstract

We performed self-consistent LMTO-ASA calculations of the electronic structure of the 1 × 1 $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ (YBCO/PBCO) superlattice, based on the local-spin-density approximation with on-site Coulomb correlation. ¿From our results, we can exclude that the experimentally observed depression of the critical temperature is originated intrinsically by a modification of the electronic structure of the CuO_2 planes. We find that the charge transfer between YBCO and PBCO layers is one order lower than the value required to explain the strong depression of both the critical temperature T_c(onset) and the zero-resistance transition temperature T_c^0, within the hole-filling model.

(to appear in Phys. Rev. B **54**)
Manuscripts available from: biagini@imoax1.unimo.it

Optical properties of isolated and interacting silicon quantum wires

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and Dipartimento di Fisica, Universitá di Modena,
via Campi 213/A, I-41100 Modena, Italy
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Abstract

We have studied the effect of hydrogen passivation and inter-wire interaction on the electronic structure and optical properties of nanoscale Si wires through two first principle techniques: LMTO-ASA and Norm-conserving Pseudopotential. We have considered free, partially and totally H-passivated [001] Si quantum wires with various rectangular cross sections; moreover we have investigated the inter-wire interaction, by varying the wire density. The optical properties have been computed by evaluating the imaginary part of the dielectric function and the absorption coefficient. We find that wires with diameters as small as 10-25 Å are actives in the visible range. Inter-wire interaction leads to the presence of localized interface states which lower the band gap energy. These results are important for the discussion about the dimensionality of confined Si quantum particles in porous Si and for the debate on quantum confinement models.

(to appear in Thin Solid Films (1996))
Manuscripts available from: ossicini@imoax1.unimo.it

Computation of the Local Electronic Density of States for all Surface Atoms in Different Microfacet Models of $TiO_2(100)1 \times 3$

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Abstract

Recently microfacets on reconstructed $TiO_2(100)1 \times 3$ have been observed with atomic resolution by scanning tunneling microscopy (Murray *et al.* 1994) and surface core-level-shift photoelectron diffraction (Hardman *et al.* 1993). Determination of the electronic structure of extended surface defects is a formidable computational problem and only now possible by using the most powerful computers.

Earlier studies, by one of the authors (Michalewicz 1994a, 1994b, Michalewicz and Priebatsch 1995), on the electronic structure of transition metal oxides with high concentration of *point defects* in a very large atomistic models of up to 500,000 atoms, have now been extended to the very large samples with *extended surface defects* such as microfacets.

We present computed results for the Local Density of States (LDOS) for up to 13 inequivalent Ti and O surface atoms in the vicinity of a microfacet, for five different models of a microfacet. This type of calculation might be useful for extracting information on atomic composition in the spectroscopic mode of operation of the Scanning Tunneling Microscope.

We also present the results of benchmark analysis of our electronic structure code on a vector-parallel computer (Cray C90). We compare vector-parallel performance with the SIMD performance (MasPar MP-1, MP-2 16K PE) and report on our efforts to implement the code on MIMD architecture (Cray T3D).

Murray, P.M.; Leibsle, F.M.; Muryn, C.A.; Fisher, H.J.; Flipse, C.F.J. and Thornton, G. 1994. *Physical Review Letters* **72**, 689.

Hardman, P.J.; Prakash, N.S.; Muryn, C.A.; Raikar, G.N.; Thomas, A.G.; Prime, A.F.; Thornton, G. and Blake, R.J. 1993. *Physical Review B* **47**, 16056.

Michalewicz, M.T. 1994a. "Massively Parallel Studies of the Electronic Structure of Disordered Micro-crystallites of Transition Metal Oxides", in *High Performance Computing 1994*, Proceedings of The Society for Computer Simulation Multiconference (San Diego, CA, Apr.10-15), A. Tentner, Ed., The Society for Computer Simulation, San Diego, 1994, 108-113.
Michalewicz, M.T. 1994b. *Computer Physics Communications* **79**, 13-23.
Michalewicz, M.T. and Priebatsch, M. 1995. *Parallel Computing* (in press).

(in High Performance Computing 1995, A. Tentner, Ed., The Society for Computer Simulations, San Diego, 1995, p.101-106)
Reprints: marek@mel.dit.csiro.au;
`http://www.mel.dit.csiro.au/~marek/papers_list.html`

Studies of the Electronic Structure of Very Large Non-periodic Atomic Systems on PVP and MPP Cray Architectures

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Abstract

A program for electronic structure computations, which scales linearly (O(N)) with the number of atoms in a system, suitable for disordered systems, transition metal oxides, interfaces, superlattices, and in general for nanometer scale engineered structures consisting of millions of atoms, has been implemented on a vector-parallel Cray C90. It runs at a speed of 8.5 GFlop/s on 16 CPUs Cray C90. We believe that the system studied using this program (1,105,920 atoms in rutile TiO_2) is the largest quantum mechanical electronic structure calculation reported so far.

We report on our experiences of porting and optimizing this code on C90 and T3D architectures.

(in Cray Users Group 1996 Spring Proceedings, Barcelona, p.88-93)
Reprints: marek@mel.dit.csiro.au;
`http://www.mel.dit.csiro.au/~marek/papers_list.html`

Rational Nano-Electronic Device Design - A definition of another Grand Challenge problem

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Abstract

We are currently witnessing rapid advances in atomistic level computations in materials science and condensed matter physics. At the same time working electronic devices are being fabricated on the nanometer scale. We will soon reach a cross-over point where the size of the modelled or simulated physical system, at the atomistic (quantum mechanical) level is the same as that of the fabricated device. It will then be possible to model operational characteristics of a nano-device with atomic resolution in quantum limits of operation in "real time". The emergence of a Rational Nanoelectronic Device Design methodology is outlined.

Many fundamental outstanding problems remain, but studies of some electronic properties, related to the characteristics of a device, for very large atomistic systems have already been done. As an example of computation we present our quantum mechanical electronic structure studies of disordered transition metal oxide systems exceeding 500 000 atoms. The model runs at a speed of 9.5 GFLOP/s on a vector-parallel Cray C90 supercomputer and takes about 400 seconds wall clock time to complete.

(in High Performance Computing-Asia '95 Electronic Proceedings,
National Center For High-Performance Computing, Taiwan, Email: hpc@nchc.gov.tw)
Reprints: marek@mel.dit.csiro.au;
`http://www.mel.dit.csiro.au/~marek/papers_list.html`

Scattering of hydrogen molecules from a reactive surface: Strong off-specular and rotationally inelastic diffraction.

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Abstract

Six-dimensional quantum dynamical calculations of the scattering of H_2 from a Pd (100) surface using a potential energy surface derived from density-functional theory calculations are presented. Due to the corrugation and anisotropy of the PES strong off-specular and rotationally inelastic diffraction is found. The dependence of the diffraction intensitities on the incident kinetic energy is closely examined. In particular we focus on the quantum oscillations for normal and off-normal incidence.

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Ab initio Molecular Dynamics Study of D_2 Desorption from Si (100)

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Abstract

Ab initio molecular dynamics calculations of deuterium desorbing from Si (100) have been performed in order to monitor the energy redistribution among the hydrogen and silicon degrees of freedom during the desorption process. The calculations show that part of the potential energy at the transition state to desorption is transferred to the silicon lattice. The deuterium molecules leave the surface vibrationally hot and rotationally cold, in agreement with experiments; the mean kinetic energy, however, is larger than found in experiments.

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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The adsorption structure of hydrogen on W(110) - back to normal

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Abstract

New structure determinations of hydrogen adsorbed on the W (110) surface using low energy electron diffraction and density functional theory calculations at monolayer coverage find a practically unreconstructed substrate on which hydrogen atoms reside in threefold coordinated hollow sites. This contradicts a long accepted and exceptional hydrogen induced registry shift of the top tungsten layer. A reinterpretation of data of the corresponding former work on the basis of an unexpected strong influence of hydrogen scattering is in agreement with our results bringing the adsorption system back to normal.

(submitted to Phys. Rev. Lett.)
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The equilibrium shape of InAs quantum dots grown on a GaAs (001) substrate

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Abstract

The equilibrium shape of strained InAs quantum dots grown epitaxially on a GaAs (001) substrate is derived as a function of volume. InAs surface energies are calculated within density-functional theory, and a continuum approach is applied for the elastic relaxation energies.

(to appear in "The Physics of Semiconductors" World Scientific, Singapore 1996)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Enhanced electron-phonon coupling at the Mo and W (110) surfaces induced by adsorbed hydrogen

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Abstract

The possible occurrence of either a charge-density-wave or a Kohn anomaly is governed by the presence of Fermi-surface nesting and the subtle interaction of electrons and phonons. Recent experimental and theoretical investigations suggest such an effect for the hydrogen covered Mo and W (110) surfaces. Using density-functional theory we examine the electronic structure and the electron-phonon coupling of these systems. Besides good agreement with the experimental phonon frequencies our study provides a characterization and quantitative analysis of an unusual scenario determining the electronic, vibrational, and structural properties of these surfaces.

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Anisotropy of growth of the close-packed surfaces of silver

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Abstract

The growth morphology of clean silver exhibits a profound anisotropy: The growing surface of Ag (111) is typically very rough while that of Ag (100) is smooth and flat. This serious and important difference is unexpected, not understood, and hitherto not observed for any other metal. Using density functional theory calculations of self-diffusion on flat and stepped Ag(100) we find, for example, that at flat regions a hopping mechanism is favored, while across step edges diffusion proceeds by an exchange process. The calculated microscopic parameters explain the experimentally reported growth properties.

(Phys. Rev. Lett. **77**, 1095 (1996).)
Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Anomalous behavior of Ru for catalytic oxidation: A theoretical study of the catalytic reaction $CO + 1/2\ O_2 \rightarrow CO_2$

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Abstract

Recent experiments revealed an anomalous dependence of carbon monoxide oxidation at Ru (0001) on oxygen pressure and a particularly high reaction rate. Below we report density functional theory calculations of the energetics and reaction pathways of the speculated mechanism. We will show that the exceptionally high rate is actuated by a weakly but nevertheless well bound (1×1) oxygen adsorbate layer. Furthermore it is found that reactions via scattering of *gas-phase* CO at the oxygen covered surface play an important role. Our analysis reveals, however, that reactions via *adsorbed* CO molecules (the so-called Langmuir-Hinshelwood mechanism) dominate.

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Local reactivity of solid surfaces

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Abstract

The quantity $w^N(\mathbf{r}) = (1/k^2 T_{\rm el})[\partial n(\mathbf{r}, T_{\rm el})/\partial T_{\rm el}]_{v(\mathbf{r}),N}$ is introduced as a convenient measure of the local isoelectronic reactivity of surfaces. It characterizes the local polarizability of the surface and it can be calculated easily. The quantity $w^N(\mathbf{r})$ supplements the charge transfer reactivity measured e.g. by the local softness to which it is closely related. We demonstrate the applicability and virtues of the function $w^N(\mathbf{r})$ for the example of hydrogen dissociation and adsorption on Pd (100).

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Paper available from: http://www.fhi-berlin.mpg.de/th/paper.html
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Non-linear electronic responses, Fukui functions and hardnesses as functionals of the ground-state electronic density

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Abstract

The exact equations for the variations of the electronic density induced by an adiabatic external potential are derived to an arbitrary perturbation order in the framework of Density-Functional-Theory. The formal solutions of these density perturbation equations are given and the exact relations between the electronic response functions and the Hohenberg-Kohn functional are derived. Using these relations, the static non-linear electronic response functions are constructed from the linear one. Non-conserving electron number perturbations are also directly included in the formalism to all perturbation orders. In this way the well-known results of the density-functional reactivity theory are generalized beyond the first and the second-order. This makes it possible to derive the exact relations between the Hohenberg-Kohn functional and the linear and non-linear Fukui responses, the non-linear Fukui functions and the non-linear hardnesses. These relations allow us to reformulate *all* the derivatives of the electronic energy relative to the external potential and to the particle number in terms of the linear response kernel and in terms of the linear Fukui function. The formalism is applied to the Thomas-Fermi-Dirac-λ von Weiszäcker model of the Hohenberg-Kohn functional. Application of this work to the microscopic calculation of Helium-Atom-Scattering cross-sections from metal surfaces will be discussed in a further publication.

(to be published in J. Chem. Phys., Sept-Oct 1996)
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Step-induced unusual magnetic properties of ultrathin Co/Cu films: ab initio study

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Abstract

We have performed *ab initio* studies to elucidate the unusual magnetic behavior recently observed in epitaxial Co films upon absorption of submonolayers of Cu and other materials. We find that a submonolayer amount of Cu on a stepped Co/Cu (100) film changes dramatically the electronic and magnetic structure of the system. The effect is mainly due to hybridization of Co and Cu d-electrons when copper forms a "wire" next to a Co step at the surface.As a result, a non-collinear arrangement of magnetic moments (switching of the easy axis) is promoted.

(submitted to Physical Review)
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Theoretical MXD-investigations on transition metal alloys containing 4d-elements

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Abstract

One of the main virtues of X-ray spectroscopy using polarized radiation is that it allows to probe magnetic properties in an element specific way. This property has been exploited in the past extensively to study the magnetism induced by magnetic neighbors in diluted and concentrated alloys, compounds and multilayer systems. Here results are presented on corresponding theoretical investigations on disordered transition metal alloys containing 4d-elements. As found before from neutron scattering studies the induced moments of normally non-magnetic alloy components turned out to vary strongly from element to element and to depend on the magnetic alloy partner. This is reflected in the corresponding magnetic X-ray dichroism spectra that are in general found to be in very satisfying agreement with recent experimental results. In contrast to the interpretation of experimental spectra no fundamental difference could be found concerning the MXD at the $L_{2,3}$-, $M_{2,3}$- and $N_{2,3}$-edges of 4d-elements.

(contribution to the XAFS-IXi, to be published in *Journal de Physique*)
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MXD–Model Calculations and a Fully Relativistic Theory for Magnetic EXAFS

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Abstract

New theoretical developments based on a fully relativistic description of magnetic dichroism (MXD) in X-ray absorption spectroscopy are presented. It is demonstrated that it is possible to achieve within this sophisticated framework an unambiguous identification of the role of exchange splitting and spin-orbit coupling for the MXD by means of model calculations. A description of this approach that consists in the separate manipulation of both sources of the MXD is presented together with several applications to K-and $L_{2,3}$-edge-spectra of transition metals. All fully relativistic calculations on the MXD have been done so far in the XANES region using the standard relativistic (κ,μ)-representation. In dealing with magnetic EXAFS it seems to be more advantageous to treat the multiple scattering for the final states in real-space adopting the (l,m_l,m_s)-representation. A corresponding generalization for the matrix inversion as well as the expansion techniques will be presented.

(contribution to the XAFS-IX, to be published in *Journal de Physique*)
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Magnetic dichroism in valence band X-ray photoemission spectroscopy

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Abstract

A fully relativistic description of spin-resolved valence band X-ray photoemission spectroscopy (VB-XPS) of magnetic solids is presented that is based on multiple scattering theory. This approach allows it to investigate for the first time possible magnetic dichroism in VB-XPS. As is demonstrated by results for $\mathrm{Co}_x\mathrm{Pt}_{1-x}$ application to disordered alloys is straightforward in the framework of the Coherent Potential Approximation (CPA) alloy theory. The spin-integrated spectra for unpolarized radiation were found to be in very satisfying agreement with corresponding experimental data. For the spin-resolved spectra a pronounced magnetic circular dichroism is predicted that should be easily observed.

(submitted to Phys. Rev. B)
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HIGHLIGHT OF THE MONTH

Orbital Functionals in Density Functional Theory: The Optimized Effective Potential Method

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The success of density functional theory hinges on the availability of good approximations for the total-energy functional. In this article we review a particular approach to the construction of approximations involving explicitly orbital-dependent functionals. The advantages of this approach over the conventional Kohn-Sham scheme are highlighted and numerical results are presented for atoms, molecules and solids.

3 Introduction: What is the optimized effective potential?

The optimized effective potential (OEP) is not a new development. In fact, its discovery [1] preceeds the development of modern density functional theory. In present-day language, the *exact* OEP should be called the *exact* Kohn-Sham (KS) potential. When it comes to approximations, however, the OEP representation of the KS potential allows for the construction of more accurate functionals than the conventional local density (LDA) or generalized gradient (GGA) approximations. In order to understand the nature of the OEP we first briefly review the basics of density functional theory (DFT).

Modern DFT is based on the celebrated theorem of Hohenberg and Kohn (HK) [2] which may be summarized by the following three statements:

1. The ground-state density ρ uniquely determines the external potential $V = V[\rho]$ as well as the ground-state wave function $\Psi[\rho]$. As a consequence, any observable of a static many-particle system is a functional of its ground state density.

2. If $\hat{T}$ denotes the kinetic energy operator of the particles and $\hat{W}_{\mathrm{Clb}}$ their mutual Coulomb interaction, the total-energy functional

$$E_{v_0}[\rho] :=< \Psi[\rho]|\hat{T} + \hat{W}_{\mathrm{Clb}} + \hat{V}_0|\Psi[\rho] > \tag{1}$$

   of a particular physical system characterized by the external potential V_0 is equal to the exact ground-state energy E_0 if and only if the exact ground-state density ρ_0 is inserted. For all other densities $\rho \neq \rho_0$ the inequality

$$E_0 < E_{v_0}[\rho] \tag{2}$$

   holds. Consequently, the exact ground-state density ρ_0 and the exact ground-state energy E_0 can be determined by solving the Euler-Lagrange equation

$$\frac{\delta}{\delta\rho(\mathbf{r})} E_{v_0}[\rho] = 0. \tag{3}$$

3. The functional

$$F[\rho] :=< \Psi[\rho]|\hat{T} + \hat{W}_{\mathrm{Clb}}|\Psi[\rho] > \tag{4}$$

   is universal in the sense that it is independent of the external potential V_0 of the particular system considered, i.e. it is of the same functional form for all systems with a fixed particle-particle interaction ($\hat{W}_{\mathrm{Clb}}$ in our case).

The proof of the HK theorem does not depend on the particular form of the particle-particle interaction. It is valid for *any* given particle-particle interaction $\hat{W}$, in particular also for $\hat{W} \equiv 0$, i.e. for non-interacting systems described by Hamiltonians of the form $\hat{H}_S = \hat{T} + \hat{V}_S$. Hence the potential $V_S(\mathbf{r})$ is uniquely determined by the ground-state density:

$$V_S(\mathbf{r}) = V_S[\rho](\mathbf{r}). \tag{5}$$

As a consequence, all single-particle orbitals satisfying the Schrödinger equation (atomic units are used throughout)

$$\left(-\frac{\nabla^2}{2} + V_S[\rho](\mathbf{r})\right)\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}) \tag{6}$$

are functionals of the density as well:

$$\varphi_j(\mathbf{r}) = \varphi_j[\rho](\mathbf{r}). \tag{7}$$

The HK total-energy functional of non-interacting particles is given by

$$E_S[\rho] = T_S[\rho] + \int \mathrm{d}^3r\, \rho(\mathbf{r}) V_S(\mathbf{r}) \tag{8}$$

where $T_S[\rho]$ is the kinetic-energy functional of non-interacting particles:

$$T_S[\rho] = \sum_{\substack{i=1 \\ \text{lowest } \varepsilon_i}}^{N} \int \mathrm{d}^3r\, \varphi_i^*[\rho](\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_i[\rho](\mathbf{r}). \tag{9}$$

We emphasize that the quantity (9) really represents a *functional of the density:* Functional means that we can assign a unique number $T_S[\rho]$ to any function $\rho(\mathbf{r})$. This is done by first calculating that very potential $V_S(\mathbf{r})$ which uniquely corresponds to $\rho(\mathbf{r})$. Several numerical schemes have been devised to achieve this task [3, 4, 5, 6, 7, 8]. Then we take this potential, solve the Schrödinger equation (6) with it to obtain a set of orbitals $\{\varphi_j(\mathbf{r})\}$ and use those to calculate the number T_S by evaluating the right-hand side of Eq. (9). As a matter of fact, by the same chain of arguments, *any orbital functional is an (implicit) functional of the density,* provided the orbitals come from a local, i.e. multiplicative potential.

Returning to the *interacting* system of interest we now define the so-called exchange-correlation (xc) energy functional by

$$E_{\mathrm{xc}}[\rho] := F[\rho] - \frac{1}{2} \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - T_{\mathrm{S}}[\rho]. \tag{10}$$

The HK total-energy functional (1) can then be written as

$$E_{v_0}[\rho] = T_{\mathrm{S}}[\rho] + \int \mathrm{d}^3r\, \rho(\mathbf{r}) v_0(\mathbf{r}) + \frac{1}{2} \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\mathrm{xc}}[\rho]. \tag{11}$$

In historical retrospective we may identify three generations of density functional schemes which may be classified according to the level of approximations used for the universal functionals $T_S[\rho]$ and $E_{\mathrm{xc}}[\rho]$.

In what we call the *first generation of DFT, explicitly* density-dependent functionals are used to approximate both $T_S[\rho]$ and $E_{\mathrm{xc}}[\rho]$. For example, the simplest and historically first approximation of this kind is the Thomas-Fermi model, where $E_{\mathrm{xc}}[\rho]$ is neglected completely and $T_S[\rho]$ is approximated by an LDA yielding

$$E_{v_0}^{\mathrm{TF}}[\rho] = \frac{3}{10} \left(3\pi^2 \right)^{2/3} \int \mathrm{d}^3r\, \rho(\mathbf{r})^{5/3} + \int \mathrm{d}^3r\, v_0(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{12}$$

as approximate expression for the total-energy functional. For functionals of this type the HK variational principle (3) can be used directly, leading to variational equations of the Thomas-Fermi type. As these equations only contain one basic variable, namely the density $\rho(\mathbf{r})$ of the system, they are readily solved numerically. The results obtained in this way, however, are generally of moderate quality.

The *second generation* of DFT employs the *exact* functional (9) for the non-interacting kinetic energy and an approximate density functional for the xc energy:

$$E^{\mathrm{KS}}_{v_0}[\rho] = T^{\mathrm{exact}}_{\mathrm{S}}[\rho] + \int \mathrm{d}^3 r\, v_0(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[\rho]. \tag{13}$$

This total-energy expression leads to the conventional Kohn-Sham version of DFT [9]. The HK variational principle (3) applied to (13) leads to a unique single-particle potential (which is commonly referred to as KS potential)

$$V_S[\rho](\mathbf{r}) = V_0(\mathbf{r}) + \int \mathrm{d}^3 r' \,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})} \tag{14}$$

such that the orbitals resulting from (6) with the potential (14) reproduce the density of the interacting system of interest.

Finally, in the *third generation, which is the OEP version of DFT,* one employs in addition to the *exact* expression for T_S also the *exact* expression for the exchange energy given by

$$E^{\mathrm{exact}}_{\mathrm{x}}[\rho] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j,k=1}^{N_\sigma} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \,\frac{\varphi^*_{j\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{15}$$

Only the correlation part of $E_{\mathrm{xc}}[\rho]$ needs to be approximated in this approach. In contrast to the conventional second-generation KS-scheme, the third generation allows for the treatment of explicitly orbital-dependent functionals for the correlation energy E_{c} as well, giving more flexibility in the construction of such approximations.

The central equation in the OEP version of DFT is still the KS equation (6) and the xc potential is still given by the functional derivative

$$V^{\mathrm{OEP}}_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})}. \tag{16}$$

The difference between the second and third generations lies in the level of approximation to the xc-energy. As a consequence of the orbital dependence of E_{xc} in the third generation of DFT the calculation of $V_{\mathrm{xc}}[\rho](\mathbf{r})$ from Eq. (16) is somewhat more complicated. A detailed derivation will be given in the following section for the spin-dependent version of DFT. The result is an integral equation determining the xc potential. This integral equation, known as the optimized effective potential equation, is very hard to solve numerically. To avoid a full-scale numerical solution, Krieger, Li and Iafrate [10, 11] have devised a semi-analytical scheme for solving the OEP integral equation approximately. This scheme is described in the following section as well. Finally a selection of numerical results for atoms, molecules and solids will be presented in the last section.

We mention that a time-dependent generalization of the OEP has recently been developed [12] to deal with explicitly time-dependent situations such as atoms in strong laser pulses [13]. In the linear-response regime this method has led to a rather successful procedure [14] to calculate excitation energies from the poles of the frequency-dependent density response. Time-dependent applications of this kind will not be discussed in the present article. The interested reader is referred to a recent review of time-dependent DFT [15].

4 Basic formalism of the OEP and KLI methods

We are going to derive the OEP equations for the spin-dependent version of DFT [16, 17], where the basic variables are the spin-up and spin-down densities $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, respectively. The latter are obtained by self-consistently solving the KS equations

$$\left(-\frac{\nabla^2}{2}+V_{S\sigma}[\rho_\uparrow,\rho_\downarrow](\mathbf{r})\right)\varphi_{j\sigma}(\mathbf{r})=\varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r})\qquad j=1,\dots,N_\sigma\qquad \sigma=\uparrow,\downarrow \tag{17}$$

where

$$\rho_\sigma(\mathbf{r})=\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2. \tag{18}$$

The Kohn-Sham potentials $V_{S\sigma}(\mathbf{r})$ may be written in the usual way as

$$V_{S\sigma}(\mathbf{r})=v_0(\mathbf{r})+\int \mathrm{d}^3r'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{\mathrm{xc}\sigma}(\mathbf{r}), \tag{19}$$

$$\rho(\mathbf{r})=\sum_{\sigma=\uparrow,\downarrow}\rho_\sigma(\mathbf{r}) \tag{20}$$

where

$$V_{\mathrm{xc}\sigma}(\mathbf{r}):=\frac{\delta E_{\mathrm{xc}}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma(\mathbf{r})}. \tag{21}$$

The starting point of the OEP method is the total-energy functional

$$\begin{aligned}E_{v_0}^{\mathrm{OEP}}[\rho_\uparrow,\rho_\downarrow] \;=\;& \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\int \mathrm{d}^3r\;\varphi_{i\sigma}^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\varphi_{i\sigma}(\mathbf{r})\\ &+\int \mathrm{d}^3r\;v_0(\mathbf{r})\rho(\mathbf{r})\\ &+\frac{1}{2}\int \mathrm{d}^3r\int \mathrm{d}^3r'\;\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &+E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]\end{aligned} \tag{22}$$

where, in contrast to ordinary spin DFT, the xc energy is an *explicit* (approximate) functional of spin orbitals and therefore only an *implicit* functional of the spin densities $\rho_\uparrow$ and $\rho_\downarrow$. In order to calculate the xc potentials from Eq. (21) we use the chain rule for functional derivatives to obtain

$$\begin{aligned}V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) \;&=\; \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta\rho_\sigma(\mathbf{r})}\\ &=\;\sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int \mathrm{d}^3r'\;\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta\rho_\sigma(\mathbf{r})}+c.c.\end{aligned} \tag{23}$$

and, by applying the functional chain rule once more,

$$V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r})=\sum_{\alpha=\uparrow,\downarrow}\sum_{\beta=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int \mathrm{d}^3r'\int \mathrm{d}^3r''\left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}[\{\varphi_{j\tau}\}]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\beta}(\mathbf{r}'')}+c.c.\right)\frac{\delta V_{S\beta}(\mathbf{r}'')}{\delta\rho_\sigma(\mathbf{r})}. \tag{24}$$

The last term on the right-hand side is readily identified with the inverse $\chi_S^{-1}(\mathbf{r},\mathbf{r}')$ of the density response function of a system of non-interacting particles

$$\chi_{S\alpha,\beta}(\mathbf{r},\mathbf{r}') := \frac{\delta\rho_\alpha(\mathbf{r})}{\delta V_{S\beta}(\mathbf{r}')}. \tag{25}$$

This quantity is diagonal with respect to the spin variables so that Eq. (24) reduces to

$$V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int \mathrm{d}^3r' \int \mathrm{d}^3r'' \left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r}'')} + c.c.\right)\chi_{S\sigma}^{-1}(\mathbf{r}'',\mathbf{r}). \tag{26}$$

Acting with the response operator (25) on both sides of Eq. (26) one obtains

$$\int \mathrm{d}^3r'\, V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}')\chi_{S\sigma}(\mathbf{r}',\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int \mathrm{d}^3r'\, \frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} + c.c.. \tag{27}$$

Finally, the second functional derivative on the right-hand side of Eq. (27) is calculated using first-order perturbation theory. This yields

$$\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} = \delta_{\alpha,\sigma}\sum_{\substack{k=1\\k\neq i}}^{\infty}\frac{\varphi_{k\sigma}(\mathbf{r}')\varphi_{k\sigma}^*(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}}\varphi_{i\sigma}(\mathbf{r}). \tag{28}$$

Using this equation, the response function

$$\chi_{S\alpha,\beta}(\mathbf{r},\mathbf{r}') = \frac{\delta}{\delta V_{S\beta}(\mathbf{r}')}\left(\sum_{i=1}^{N_\alpha}\varphi_{i\alpha}^*(\mathbf{r})\varphi_{i\alpha}(\mathbf{r})\right) \tag{29}$$

is readily expressed in terms of the orbitals as

$$\chi_{S\sigma}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N_\sigma}\sum_{\substack{k=1\\k\neq i}}^{\infty}\frac{\varphi_{i\sigma}^*(\mathbf{r})\varphi_{k\sigma}(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{i\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}} + c.c.. \tag{30}$$

Inserting (28) and (30) in Eq. (27), we obtain the standard form of the OEP integral equation:

$$\sum_{i=1}^{N_\sigma}\int \mathrm{d}^3r' \left(V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}(\mathbf{r}') - u_{\mathrm{xc}i\sigma}(\mathbf{r}')\right) G_{Si\sigma}(\mathbf{r}',\mathbf{r})\,\varphi_{i\sigma}(\mathbf{r})\varphi_{i\sigma}^*(\mathbf{r}') + c.c. = 0 \tag{31}$$

where

$$u_{\mathrm{xc}i\sigma}(\mathbf{r}) := \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})}\frac{\delta E_{\mathrm{xc}}^{\mathrm{OEP}}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\sigma}(\mathbf{r})} \tag{32}$$

and

$$G_{Si\sigma}(\mathbf{r},\mathbf{r}') := \sum_{\substack{k=1\\k\neq i}}^{\infty}\frac{\varphi_{k\sigma}(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}}. \tag{33}$$

The derivation of the OEP integral equation (31) described here was first given by Görling and Levy [18]. It is important to note that the same expression results [1, 19, 10, 20] if one demands that the local one-particle potential appearing in Eq. (17) be the *optimized* one yielding orbitals minimizing the total-energy functional (22), i.e. that

$$\left.\frac{\delta E_{v_0}^{OEP}}{\delta V_{S\sigma}(\mathbf{r})}\right|_{V_S=V^{OEP}} = 0. \tag{34}$$

This equation is the historical origin [1] of the name *optimized effective potential.*

In order to use the OEP, one has to solve the OEP integral equation (31) for the xc potential $V_{\mathrm{xc}\sigma}^{\mathrm{OEP}}$ in each iterative step of the KS self-consistency cycle. This is a rather demanding task and has been achieved so far only for systems of high symmetry such as spherical atoms [19, 10, 21] and for solids within the linear muffin tin orbitals atomic sphere approximation [22, 23, 24].

To avoid the full-scale numerical solution of the OEP integral equation Krieger, Li and Iafrate (KLI) [11] suggested a semi-analytical approximation. It can be derived by replacing the energy denominators in the Green's function type quantity (33) by an average energy difference independent of i and k:

$$G_{\mathrm{s}i\sigma}(\mathbf{r},\mathbf{r}') \approx \frac{1}{\triangle\epsilon}\left(\delta\left(\mathbf{r}-\mathbf{r}'\right) - \varphi_{i\sigma}(\mathbf{r})\varphi_{i\sigma}^*(\mathbf{r}')\right). \tag{35}$$

Substituting this into the integral equation (31) and performing some algebra one arrives at the equation

$$V_{\mathrm{xc}\sigma}^{\mathrm{KLI}}(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2\left[U_{\mathrm{xc}i\sigma}(\mathbf{r}) + \left(\bar{V}_{\mathrm{xc}i\sigma} - \bar{U}_{\mathrm{xc}i\sigma}\right)\right] \tag{36}$$

where $U_{\mathrm{xc}i\sigma}(\mathbf{r}) = \frac{1}{2}(u_{\mathrm{xc}i\sigma}(\mathbf{r}) + u_{\mathrm{xc}i\sigma}^*(\mathbf{r}))$ and $\bar{U}_{\mathrm{xc}j\sigma}$ denotes the average value of $U_{\mathrm{xc}j\sigma}(\mathbf{r})$ taken over the density of the $j\sigma$ orbital, i.e.

$$\bar{U}_{\mathrm{xc}j\sigma} = \int \mathrm{d}^3r\ |\varphi_{j\sigma}(\mathbf{r})|^2 U_{\mathrm{xc}j\sigma}(\mathbf{r}) \tag{37}$$

and similarly for $\bar{V}_{\mathrm{xc}i\sigma}$. In contrast to the exact integral equation (31) the KLI equation (36) can be solved explicitly for $V_{\mathrm{xc}\sigma}$ by multiplication with $|\varphi_{i\sigma}(\mathbf{r})|^2$ and subsequent integration. This leads to an $(N_\sigma - 1)\times(N_\sigma - 1)$ system of linear equations for the unknown constants $\left(\bar{V}_{\mathrm{xc}i\sigma} - \bar{U}_{\mathrm{xc}i\sigma}\right)$:

$$\sum_{i=1}^{N_\sigma - 1}\left(\delta_{ji} - M_{ji\sigma}\right)\left(\bar{V}_{\mathrm{xc}i\sigma} - \bar{U}_{\mathrm{xc}i\sigma}\right) = \bar{V}_{\mathrm{xc}j\sigma}^S - \bar{U}_{\mathrm{xc}j\sigma} \qquad j = 1,\ldots,N_\sigma - 1 \tag{38}$$

with

$$M_{ji\sigma} := \int \mathrm{d}^3r\ \frac{|\varphi_{j\sigma}(\mathbf{r})|^2|\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} \tag{39}$$

and

$$\bar{V}_{\mathrm{xc}j\sigma}^S(\mathbf{r}) := \int \mathrm{d}^3r\ \frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N}|\varphi_{i\sigma}(\mathbf{r})|^2 U_{\mathrm{xc}i\sigma}(\mathbf{r}). \tag{40}$$

It is an important property of the KLI approximation that it is exact for two-particle systems, where one has only one electron per spin projection. In this case, the OEP integral equation (31) may be solved exactly to yield (36).

At first sight, the KLI approximation (35) might appear rather crude. The final result (36) for the KLI potential, however, can also be understood [11] as a well-defined mean-field approximation. Explicit calculations on atoms performed in the x-only limit [25] show that the KLI approximation yields excellent results with, e.g., ground-state energies differing only by a few ppm from the much more time-consuming exact solutions of the full integral equation (31). We will give numerical examples in the next section.

To conclude this section we describe (without proof) some exact properties of the OEP method and the KLI approximation.

1. **Asymptotics**
   For finite systems, both the full OEP and the KLI potential fall of as $-1/r$ for $r \to \infty$ [10] if the exact expression (15) for the exchange-energy functional is employed. The asymptotic behaviour of the correlation potential is equal to that of the function $u_{\mathrm{c,max}\sigma}(\mathbf{r})$ corresponding to the highest occupied orbital.

2. **Freedom of self-interaction**
   If the employed xc-energy functional cancels the self-interaction of the Hartree term, this property is preserved by the KLI approximation. Thus x-only OEP and x-only KLI schemes are self-interaction free. It has to be noted, however, that the inclusion of an LDA-correlation-energy functional might introduce a self-interaction error again.

3. **Derivative discontinuities**
   An important property of the *exact* xc potential is that it exhibits discontinuities as a function of particle number N at integer values of N. This has important consequences for the values of band gaps in insulators and semi-conductors (for a detailed description see e.g. [26]): The correct value E^g of the gap is obtained by adding the discontinuity Δ_{xc} of the xc potential to the KS gap, i.e. , $E^g = E^g_{\mathrm{KS}} + \Delta_{\mathrm{xc}}$. Neither the LDA nor the GGAs reproduce this discontinuity. To date, the OEP and the KLI potential are the only known approximations of $V_{\mathrm{xc}}(\mathbf{r})$ that reproduce this discontinuity [10].

Table 1: *Various self-consistently calculated x-only results for the Ar atom. All values in atomic units.*

	OEP	KLI	B88	xPW91	xLDA
E_{TOT}	-526.8122	-526.8105	-526.7998	-526.7710	-524.5174
ε_{1s}	-114.4524	-114.42789	-114.1890	-114.1887	-113.7159
ε_{2s}	-11.1534	-11.1820	-10.7911	-10.7932	-10.7299
ε_{2p}	-8.7339	-8.7911	-8.4107	-8.4141	-8.3782
ε_{3s}	-1.0993	-1.0942	-0.8459	-0.8481	-0.8328
ε_{3p}	-0.5908	-0.5893	-0.3418	-0.3441	-0.3338
ε_{4s}	-0.1607	-0.1616	-0.0106	-0.0122	-0.0014
$< r^2 >$	1.4465	1.4467	1.4791	1.4876	1.4889
$< r^{-1} >$	3.8736	3.8738	3.8731	3.8729	3.8648
$\rho(0)$	3839.8	3832.6	3847.3	3847.0	3818.7

5 Selected Results

5.1 Atomic and molecular systems

We begin with a comparison of x-only results. In an x-only world, the OEP represents the *exact* KS potential of DFT and can therefore serve as a standard to compare approximations with. In Table 1 we show as a typical example various results for the argon atom obtained with different x-only methods. Besides the exact OEP and KLI methods described above, we also list results from conventional KS-DFT obtained with the x-energy-functional approximations due to Becke (B88) [27], Perdew and Wang (PW91) [28] and from the well-known x-only LDA approximation. The KLI results given in the second column of Table 1 clearly demonstrate the high quality of the KLI approximation as all results differ only slightly from the exact OEP ones. For all standard DFT methods, the disagreement is much more pronounced, especially for the highest occupied orbital energies and *even more so for the unoccupied ones.* The reason for this may be seen from the plots of the x-potentials shown in Figures 1 and 2: The KLI potential is much closer to the exact OEP, reproducing the so-called inter-shell peaks, which are missing in the conventional KS approximations, and furthermore the correct $-1/r$ decay of $V_{\mathrm{x}}(\mathbf{r})$ for large r. This latter property is clearly visible from the plot in Figure 2, where we show $-V_{\mathrm{x}}(\mathbf{r})$ on a logarithmic scale. None of the standard KS potentials decays in a straight

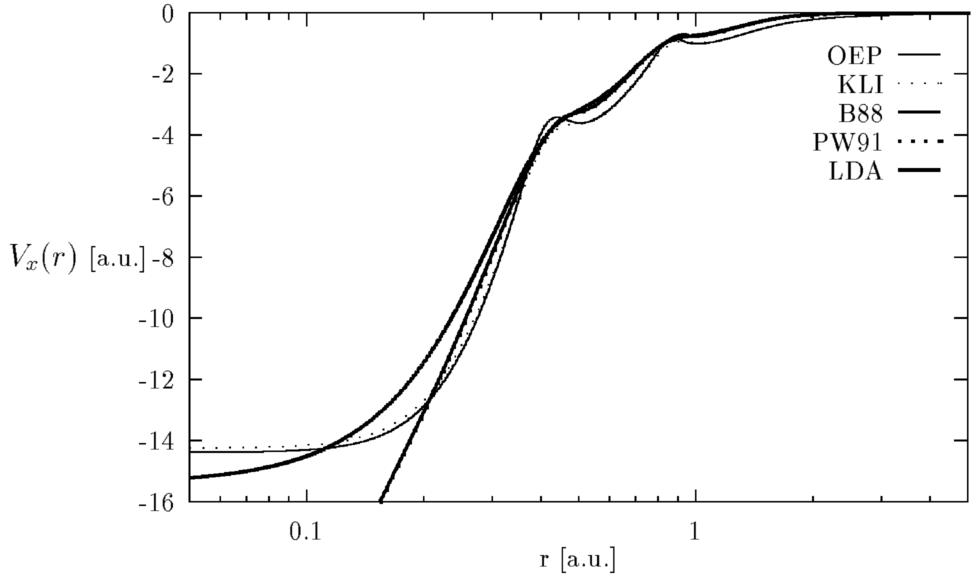

Figure 1: *Exchange potentials $V_x(\mathbf{r})$ of the Ar atom from various self-consistent calculations.*

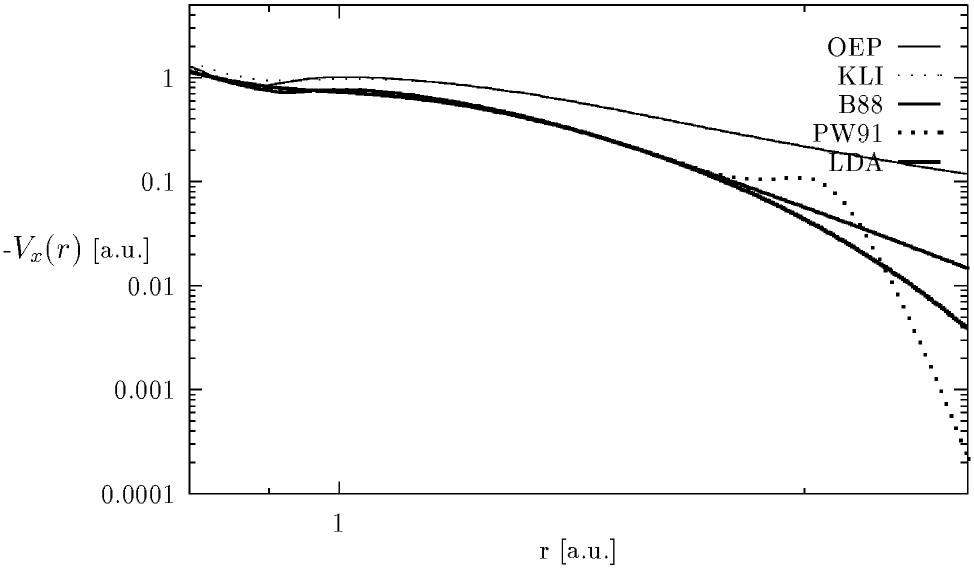

Figure 2: *Exchange potentials $-V_x(\mathbf{r})$ of the Ar atom from various self-consistent calculations in the valence region.*

line with the proper slope as the OEP and KLI potentials do.

It has been shown [20, 32, 33] that the most suitable correlation-energy functional to be included into the KLI scheme is the one developed by Colle and Salvetti (CS) [34, 35]. It is given by

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{CS}}[\{\varphi_{i\sigma}\}] \;=\; & -ab\int \mathrm{d}^3r\; \gamma(\mathbf{r})\xi(\mathbf{r})\Bigg[\sum_{\sigma}\rho_{\sigma}(\mathbf{r})\sum_{i}\,|\nabla\varphi_{i\sigma}(\mathbf{r})|^2 \;-\; \frac{1}{4}\,|\nabla\rho(\mathbf{r})|^2 \\ & -\frac{1}{4}\sum_{\sigma}\rho_{\sigma}(\mathbf{r})\triangle\rho_{\sigma}(\mathbf{r}) \;+\; \frac{1}{4}\rho(\mathbf{r})\triangle\rho(\mathbf{r})\Bigg] - a\int \mathrm{d}^3r\; \gamma(\mathbf{r})\frac{\rho(\mathbf{r})}{\eta(\mathbf{r})}, \qquad (41) \end{aligned}$$

Table 2: *Total absolute ground-state energies for first-row atoms from various self-consistent calculations [20]. Quantum chemistry (QC) values from [29].* $\bar{\Delta}$ *denotes the mean absolute deviation from the exact non-relativistic values [30]. All numbers in atomic units.*

	KLICS	LDA	BLYP	PW91	QC	exact
He	2.9033	2.8348	2.9071	2.9000	2.9049	2.9037
Li	7.4829	7.3440	7.4827	7.4742	7.4743	7.4781
Be	14.6651	14.4472	14.6615	14.6479	14.6657	14.6674
B	24.6564	24.3536	24.6458	24.6299	24.6515	24.6539
C	37.8490	37.4700	37.8430	37.8265	37.8421	37.8450
N	54.5905	54.1368	54.5932	54.5787	54.5854	54.5893
O	75.0717	74.5274	75.0786	75.0543	75.0613	75.067
F	99.7302	99.1142	99.7581	99.7316	99.7268	99.734
Ne	128.9202	128.2335	128.9730	128.9466	128.9277	128.939
$\bar{\Delta}$	0.0047	0.3795	0.0108	0.0114	0.0045	

where

$$\gamma(\mathbf{r}) = 4\,\frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho(\mathbf{r})^2}, \tag{42}$$

$$\eta(\mathbf{r}) = 1 + d\rho(\mathbf{r})^{-\frac{1}{3}}, \tag{43}$$

$$\xi(\mathbf{r}) = \frac{\rho(\mathbf{r})^{-\frac{5}{3}} e^{-c\rho(\mathbf{r})^{-\frac{1}{3}}}}{\eta(\mathbf{r})}. \tag{44}$$

The constants a, b, c and d are given by $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$.

In Table 2 we compare total ground-state energies of first-row atoms calculated self-consistently with various approximations. The first column, headed KLICS, shows the results from the KLI method employing the exact exchange energy functional (15) plus the CS-correlation energy functional while the next columns show conventional KS results obtained with the x-energy functional due to Becke [27] combined with the c-energy functional from Lee, Yang and Parr [36], denoted as BLYP, and from the generalized gradient approximation due to Perdew and Wang [28], referred to as PW91. The quantum chemistry values, headed QC, are based on configuration interaction calculations [29]. The exact non-relativistic energies, i.e. the experimental values with relativistic effects subtracted, have been taken from [30]. The mean absolute deviations of the calculated from the exact values, denoted by $\bar{\Delta}$, are about the same for the KLICS and QC approaches,

Table 3: *Ionization potentials of neutral atoms, calculated from the highest occupied orbital energies [20].* $\bar{\Delta}$ *denotes the mean absolute deviation from the experimental values, taken from [31]. All values in atomic units.*

	KLICS	LDA	BLYP	PW91	experiment
He	0.945	0.570	0.585	0.583	0.903
Li	0.200	0.116	0.111	0.119	0.198
Be	0.329	0.206	0.201	0.207	0.343
B	0.328	0.151	0.143	0.149	0.305
C	0.448	0.228	0.218	0.226	0.414
N	0.579	0.309	0.297	0.308	0.534
O	0.559	0.272	0.266	0.267	0.500
F	0.714	0.384	0.376	0.379	0.640
Ne	0.884	0.498	0.491	0.494	0.792
Na	0.189	0.113	0.106	0.113	0.189
Mg	0.273	0.175	0.168	0.174	0.281
Al	0.222	0.111	0.102	0.112	0.220
Si	0.306	0.170	0.160	0.171	0.300
P	0.399	0.231	0.219	0.233	0.385
S	0.404	0.228	0.219	0.222	0.381
Cl	0.506	0.305	0.295	0.301	0.477
Ar	0.619	0.382	0.373	0.380	0.579
$\bar{\Delta}$	0.030	0.176	0.183	0.177	

while they are about twice as high for the GGAs and about a factor of 80 higher in the LDA. We emphasize that the numerical effort involved in the KLICS scheme for atoms is only slightly higher than in the LDA and GGA schemes. Apart from total energies, the highest occupied orbital energies, which should be equal to the exact ionization potential in an exact implementation of DFT, are much closer to the experimental ionization potentials in the KLICS scheme than in the conventional KS approaches. This is shown in Table 3: All the conventional KS calculations are inadequate, the numbers are off by about 100%.

A similar picture is found for molecules. The KLICS highest occupied orbital energies

Table 4: *Energies of the highest occupied molecular orbitals of LiH, BH and FH from various calculations. The KLICS, PW91 and xcLDA results have been obtained with our basis-set-free numerical code at experimental bond lengths from [37]. The exact values of the ionization potential are from [37]. All numbers in atomic units.*

	KLICS	PW91	xcLDA	exact
LiH	-0.3224	-0.1623	-0.1613	-0.283
BH	-0.3698	-0.2052	-0.2031	-0.359
FH	-0.6772	-0.3577	-0.3608	-0.589

listed in Table 4 for some diatomic molecules are in much better agreement with the experimental values than the conventional LDA and GGA schemes. We conclude that orbital energies are universally improved for atoms and molecules in the KLICS approach. This statement, however, is not true for molecular total energies as can be seen from the dissociation energies listed in Table 5.

Similar to Hartree-Fock, the dissociation energies of some molecules as calculated within the KLICS approximation are seriously in error. Since the corresponding *atomic* ground-state energies given above are of excellent quality, the error must be due to correlation effects present in molecules only. In particular, the left-right correlation error, well known in HF theory, also occurs in DFT when the exact Fock expression for E_{x} is employed. Apparently this error is not sufficiently corrected for by the Colle-Salvetti funtional. The PW91 and LDA results are clearly much better. The fact that exchange effects are treated only approximately in these approaches seems to be an advantage. Therefore, the construction of correlation functionals better adapted to correct the left-right deficiency of the exact exchange energy functional is necessary. Work along these lines is in progress. A detailed study of x-only KLI results for molecules may be found in [32].

5.2 Solids

As pointed out in the previous sections, the OEP integral equation can be solved for spherically symmetric systems. This fact was exploited by Kotani [22, 23, 24], who implemented the exact exchange OEP into the tight-binding linear muffin-tin orbital method in the atomic sphere approximation (TB-LMTO-ASA) [42, 43, 44]. Starting point is the chain-rule relation

$$\frac{\delta E_{\mathrm{xc}}[\{\varphi\}]}{\delta V_S(\mathbf{r})} = \int d^3r' \underbrace{\frac{\delta E_{\mathrm{xc}}[\{\varphi\}]}{\delta \rho(\mathbf{r}')}}_{=V_{\mathrm{xc}}(\mathbf{r}')} \frac{\delta \rho(\mathbf{r}')}{\delta V_S(\mathbf{r})}. \tag{45}$$

Table 5: *Dissociation energies of the closed-shell-first-row dimers calculated at experimental bond lengths from [37], except for HF, where the used bond lengths were* 1.4 *a.u. for* H_2, 5.051 *a.u. for* Li_2, 4.6 *a.u. for* Be_2, 2.348 *a.u. for* C_2, 2.068 *a.u for* N_2 *and* 2.668 *a.u. for* F_2. *Experimental values calculated from [37] by the method used in [38], except for* H_2, *where the exact value is from [39]. HF results calculated from values given in [40, 41]. All values calculated with basis-set free, fully numerical codes and given in* 10^{-3} *atomic units.*

	HF	KLICS	LDA	PW91	experiment
H_2	133.630	171.349	179.897	170.657	174.475
Li_2	17.0	32.4	37.9	33.4	39.3
Be_2	-12.3	-10.5	20.5	16.0	3.8
C_2	29.4	74.8	267.5	239.1	233.5
N_2	191.1	282.7	427.1	387.4	363.9
F_2	-45	-33	125	107	62.1

Due to the spherical symmetry inside the atomic spheres within the ASA this integral equation can be solved numerically for the xc potential $V_{\mathrm{xc}}(\mathbf{r}')$. The functional derivatives with respect to the potential are calculated by differentiating E_{xc} and $\rho(\mathbf{r})$ with respect to the LMTO-parameters and the latter with respect to the potential.

Eq. (45) is equivalent to the OEP integral equation, which can easily be seen by applying the chain-rule of functional derivatives on the left-hand side of Eq. (45) leading to

$$\frac{\delta E_{\mathrm{xc}}[\{\varphi\}]}{\delta V_S(\mathbf{r})} = \sum_i \int \mathrm{d}^3 r' \, \frac{\delta E_{\mathrm{xc}}[\{\varphi\}]}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta V_S(\mathbf{r})} + c.c. \tag{46}$$

where

$$\frac{\delta \varphi_i(\mathbf{r})}{\delta V_S(\mathbf{r}')} = G_{Si}(\mathbf{r}, \mathbf{r}')\varphi_i(\mathbf{r}), \tag{47}$$

with the KS Green's function G_{Si} defined in Eq. (33). The functional derivative of $\rho(\mathbf{r}')$ with respect to $V_S(\mathbf{r})$ can be identified with the KS response function

$$\frac{\delta \rho(\mathbf{r}')}{\delta V_S(\mathbf{r})} = \chi_S(\mathbf{r}', \mathbf{r}) = \sum_{i=1}^{N} G_{Si}(\mathbf{r}', \mathbf{r})\varphi_i^*(\mathbf{r}')\varphi_i(\mathbf{r}) + c.c.. \tag{48}$$

Inserting (46) and (47) on the left-hand side and (48) on the right-hand side of Eq. (45) and using the definition of the $u_{\mathrm{xc}i}(\mathbf{r})$, Eq. (32), one recovers the OEP integral equation (31).

Kotani added an LDA correlation energy functional, using the von Barth-Hedin parametrization, and applied this method (EXX, for exact exchange) to insulators [22], semiconductors [23] and most recently to metals [24]. Some results for insulators and semiconductors are given in Tables 6 and 7. The energies found for metals are in good agreement with LDA results.

Another approach was devised by Bylander and Kleinman [45]. They implemented the KLI approximation within a pseudo-potential framework. As in the previous method, correlation effects were taken into account through an ordinary LDA, which was added to the KLI exchange-potential. The results for Ge are given in Table 7.

Table 6: *Energy gaps (in eV) at high-symmetry points for MgO and CaO from Ref. [22]*

		LDA	EXX	APW-LDA	Hartree-Fock	experiment
MgO	Direct Gap					
	Γ	4.64	6.21	4.7	25.3	7.833
	X	13.56	15.23	10.2	17.0	
	L	12.91	14.33	8.3	21.4	
CaO	Direct Gap					
	Γ	4.30	6.47	4.4	15.8	7.09
	X	4.30	7.40	3.9	19.9	
	L	7.78	10.12	7.9	21.9	
	Indirect Gap					
	$\Gamma - X$	3.96	6.97	3.5	18.7	

Table 6 shows the results of the EXX method for MgO and CaO. The values of the gap obtained with this method lie inbetween the LDA and the HF results and are in much better agreement with the experimental values. It has to be noted that the derivative discontinuities, which can in principle be calculated with the EXX method, are not taken into account here. The width of the oxygen ($2p$) states is reduced with respect to an LDA calculation, which is caused by the self-interaction cancellation of the EXX method making these states more localized. Furthermore the potential within the atomic spheres displays more structure than the corresponding LDA potential [22]. This is analogous to the inter-shell peaks discussed above for atoms.

In Table 7 the results for Si, Ge and diamond are compared for various schemes, respectively. All energies are relative to the top of the valence band which, in these systems, is the $\Gamma_{25'}$ state. Compared with the LDA results, the energies of the conduction band are consistently shifted upwards, i.e. towards the HF values, by the OEP method. As before, the overall agreement with experiment is much better in the OEP schemes than in LDA or HF. Once again, the discontinuity of the xc potential, although it can be calculated within the OEP method, was *not* taken into account in these calculations.

The importance of this discontinuity was estimated by Li, Krieger, Norman and Iafrate [47], who applied the OEP and the KLI approximately to a Perdew-Zunger SIC-LDA. Results for the energy gaps of noble-gas solids and NaCl are given in Table 8. It is clearly visible that the values of $(E^g_{\mathrm{KS}} + \Delta_{xc})$ are in much better agreement with experiment than the mere KS gaps.

Table 7: *Comparison of the KS-eigenvalues (in eV) relative to the top of the valence band ($\Gamma_{25v'}$) for Si, Ge and diamond. The LDA, EXX and also the experimental values are taken from Ref. [23]. HF values are from Ref. [46]. KLI values are from Ref. [45].*

		LDA	EXX	HF	KLI	experiment
Si	*gap*	0.45	1.93			1.17
	Γ_{15c}	2.65	3.79	8.7		3.4
	$\Gamma_{2c'}$	3.07	4.43	9.3		4.2
	L_{1c}	1.41	2.65			2.1, 2.4 ± 0.15
	L_{3c}	3.22	4.31			4.15 ± 0.1
	Γ_{1v}	-12.07	-11.35			-12.5 ± 0.6
	X_{4v}	-2.92	-2.46			-2.9, -3.3 ± 0.2
	$L_{3v'}$	-1.20	-0.91			-1.2 ± 0.2, 1.5
Ge	Γ_{15c}	2.70	3.55	7.9		3.24
	$\Gamma_{2c'}$	0.40, -0.20[a]	1.90	4.3	1.239	0.98
	$L_{1c}(gap)$	0.32	1.57		0.796	0.87, 0.84[b]
	L_{3c}	3.67	4.43			4.3
	X_{1c}	0.630			0.933	1.3 ± 0.2[b]
	Γ_{1v}	-12.68	-12.01			-12.6 ± 0.3
	L_{1v}	-7.62	-6.99			-7.7 ± 0.2, -7.4 ±0.2
	$L_{3v'}$	-1.40	-1.15			-1.4 ± 0.2
diamond	*gap*	4.00	5.12			5.48
	Γ_{15c}	5.61, 5.7[c]	6.61	14.6		7.3
	$\Gamma_{2c'}$	13.50,13.4[c]	14.04	23.7		15.3 ± 0.5
	Γ_{1v}	-21.6	-21.4			-24.2 ± 1, -21 ± 1
	L_{1v}	-13.65	-13.09			-12.8 ± 0.3

[a] *conventional LDA in TB-LMTO-ASA from [46]*

[b] *values are taken from [45]*

[c] *conventional LDA-pseudopotential calculation from [45]*

Table 8: *Gap energies (in eV) of noble-gas solids and NaCl. The values in parentheses are calculated without the derivative discontinuity (from Ref. [47]).*

	LDA	OEP	KLI	SIC	experiment
		$E^g(E^g_{\mathrm{KS}})$	$E^g(E^g_{\mathrm{KS}})$		
Ne	11.5	20.9 (15.2)	20.8 (15.2)	22.2	21.4
Ar	8.2	13.1 (9.7)	13.1 (9.7)	15.2	14.2
Kr	6.8	11.1 (8.0)	10.8 (7.9)	13.6	11.6
Xe	5.8	9.5 (6.9)	9.0 (6.7)		9.8
NaCl	5.5	9.5 (6.3)	9.5 (6.4)	10.0	9.0

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