”QUANTUM THEORY OF SOLIDS”

QTS-5 WORKSHOP IN ÅRHUS 18-20 MAY 2009

(http://www.phys.au.dk/qts5)

Program and Abstracts

AARHUS UNIVERSITET

Workshop:”Quantum Theory of Solids” (QTS-5) in Århus 18-20 May 2009.

The fifth workshop on “Quantum Theory of Solids” (QTS-5) will be held at the Department of Physics and Astronomy, University of Aarhus, 18-20 May 2009. The main theme of the meeting will be *correlations*, electron-electron as well as electron-hole correlations in f-electron materials, transition-metal oxides and in semiconductors. New developments in GW, DMFT, SIC, TDDFT, BSE methods and recent progress in the theory of diluted magnetic semiconductors will be discussed. Also some other aspects of application of quantum theory of electrons will be included, such as reactions at surfaces.

Organizers: N.E. Christensen (nec@phys.au.dk) and A. Svane (svane@phys.au.dk)

Workshop: ”Quantum Theory of Solids” (QTS-5) in Århus 18-20 May 2009.

Participants	**Affiliation**
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O.K. Andersen	Max Planck Institut FKF, Stuttgart, Germany
V. Antonov	Max Planck Institut FKF, Stuttgart, Germany
S. Biermann	Ecole Polytechnique, Palaiseau, France
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O. Eriksson	Uppsala University, Uppsala, Sweden
L. Errico	National University of La Plata, La Plata, Argentina
J. Frantti	Helsinki University of Technology, Helsinki, Finland
Y. Fujoka	Helsinki University of Technology, Helsinki, Finland
M. Gatti	Ecole Polytechnique, Palaiseau, France
I. Gorczyca	Inst.of High Pressure Physics, Academy of Sciences, Warsaw, Poland
E.K.U. Gross	Freie Universität, Berlin, Germany
O. Gunnarsson	Max Planck Institut FKF, Stuttgart, Germany
B. Hammer	University of Aarhus, Århus, Denmark
P. Hyldgaard	Chalmers Univ. Tech., Göteborg, Sweden
H. Høgh Kristoffersen	University of Aarhus, Århus, Denmark
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D.L. Novikov	United Technologies Research Center, East Hartford, Connecticut, USA
P.M. Oppeneer	Uppsala University, Uppsala, Sweden
L. Petit	Universty of Aarhus, Århus, Denmark
A. Postnikov	Paul Verlaine University, Metz, France
S. Satpathy	University of Missouri, Colombia, MO, USA
S. Savrasov	University of California, Davis, CA (USA)
M. van Schilfgaarde	Arizona State University, Tempe, AZ (USA)
J. Stausholm-Møller,	University of Aarhus, Århus, Denmark
A. Svane	University of Aarhus, Århus, Denmark
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Organizers: N.E. Christensen (nec@phys.au.dk) and A. Svane (svane@phys.au.dk)

Workshop: ”Quantum Theory of Solids” (QTS-5) in Århus 18-20 May 2009.

Invited speakers	Title of talk
O.K. Andersen	pd Wannier functions, bands and magnetism in FeAs materials
M. van Schilfgaarde	Magnetic exchange interactions in the Quasiparticle Self-Consistent GW appr.
S. Savrasov	Electronic and exchange interactions in superconducting pnictides
R.C Albers	DMFT Electronic-Structure Calculations: Fact or Fiction
A. Svane	Actinides: Total energy and GW calculations
J. Kudrnovsky	Electronic, magnetic, transport properties (Cu,Ni)MnSb Heusler alloys
C. Ambrosch-Draxl	Strongly bound electron-hole pairs
G.K.H. Madsen	Electronic-structure theory of thermoelectric materials
A. Postnikov	Impurity vibration modes in semiconductors
O. Gunnarsson	Electron-phonon coupling in correlated systems
L. Nordström	Polarisations of transition metals
W. Temmerman	Disordered local magnetic moments in 3d-monoxides and heavy 4fs
M. Lüders	The flavours of SIC
E.K.U. Gross	Ab-initio theory of superconductivity
L. Errico	Electric-field gradients at impurities in oxides from first principles
R. Laskowski	BSE and LDA+U calculations for delafossites and ZnO
K. Köpernik	Recent applications of LSDA+U: An analysis of the method
P.M. Oppeneer	Electronic structure of URu_2Si_2 and correlated Pu materials
B. Hammer	Modeling the surface reactivity of bulk-reduced rutile TiO_2
S. Biermann	Electronic correlations from a dynamical mean field perspective
S. Satpathy	Electronic structure of the perovskite oxide interfaces
M. Gatti	Understanding correlations in VO_2 from first principles
L. Petit	Electronic Phase Diagram of Rare Earth materials
J. Frantti	Polarization rotation in ferroelectrics
E. Kotomin	Hybrid functional calculations of point defects in perovskites
G. Zwicknagl	Heavy quasiparticles, instabilities and co-operative phenomena in f- el. systems
W.R.L Lambrecht	Electr. Struct., magnetism and phonons in RE nitrides, Gd-pnictides, Eu-chalcogenides
P. Hyldgaard	Van der Waals interactions in Sparse Matter
M. Alouani	Tunneling magnetoresistance of Fe/MgO/Fe junctions
O. Eriksson	Data mining electronic structures for novel materials
V. Antonov	Electronic structure and x-ray magnetic circular dichroism in $CeFe_2$

Posters

I. Gorczyca	Calculations of the band structure of In-containing nitride alloys
J. Martinez	Ab-initio calculations of FCC-FeMn alloys with the $L1_0$ structure
M. Taylor	Ab-initio study of vacancies in cubic zirconia
Z. Szotek	Structural phase transitions and band gaps in $Mg_xZn_{1-x}O$ from first principles
M. Renteria	APW+lo and TDPAC study of EFG at cation sites of $^{44}Ti(EC)^{44}Sc$-doped Sc_2O_3

Organizers: N.E. Christensen (nec@phys.au.dk) and A. Svane (svane@phys.au.dk)

PROGRAM

“QTS-5”. Program for Monday 18.05.2009.

- 8:15-8:30: Opening of meeting. N.E. Christensen.
- 8:30- 9:10: “O. Gunnarsson: “Electron-phonon coupling in correlated systems”
- 9:10- 9:50: E.K.U. Gross: “Ab-initio theory of superconductivity”
- 9:50- 10:30: S. Savrasov: “Electronic and exchange interactions in superconducting pnictides”
- 10:30-11:00: Coffee
- 11:00-11:40: W.R.L. Lambrecht: “Electronic structure, magnetism and phonons in RE nitrides, Gd-pnictides and Eu-chalcogenides”
- 11:40- 12:20: A. Postnikov: “Impurity vibration modes in semiconductors”
- 12:20-13:30: Lunch
- 13:30-14:10: O.K. Andersen: “pd Wannier functions, bands and magnetism in FeAs materials”
- 14:10-14:50: J. Kudrnovsky: “Electronic, magnetic, and transport properties of (Cu,Ni)MnSb Heusler alloys”
- 14:50-15:10: Coffee
- 15:10-15:50: L. Errico: “ Fe doped TiO2 and SnO2: Local structure and magnetic behaviour”
- 15:50-16:30: B. Hammer: “Modeling the surface reactivity of bulk-reduced rutile TiO2”
- 16:30-17:10: S. Satpathy: “Electronic structure of the perovskite oxide interfaces”
- 17:20-19:00: Poster- and beer session

“QTS-5”. Program for Tuesday 19.05.2009.

- 8:30- 9:10: M. van Schilfgaarde: “Magnetic exchange interactions in the Quasiparticle Self-consistent GW approximation”
- 9:10- 9:50: M. Lueders: “The flavours of SIC”
- 9:50- 10:30: W. Temmerman: “Disordered local magnetic moments in 3d-monoxides and heavy 4fs”
- 10:30-11:00: Coffee
- 11:00-11:40: S. Biermann: “Electronic Correlations from a dynamical mean mean field perspective”
- 11:40- 12:20: R.C. Albers: “DMFT Electronic-Structure Calculations; Fact or Fiction”
- 12:20-13:30: Lunch
- 13:30-14:10: A. Svane: “Actinides: Total energy and GW calculations”
- 14:10-14:50: M. Gatti: “Understanding correlations in VO2 from first principles”
- 14:50-15:10: Coffee
- 15:10-15:50:P.M. Oppeneer: “Electronic structure of URu2Si2 and correlated Pu materials”
- 15:50-16:30: C. Ambrosch-Draxl: “Strongly bound electron-hole pairs”
- 16:30-17:10: R. Laskowski: “BSE and LDA+U calculations for delefossites and ZnO”
- 17:10-17:50: V. Antonov: “Electronic structure and x-ray magnetic circular dichroism in CeFe2”
- 18:30: Bus departure for conference dinner

“QTS-5”. Program for Wednesday 20.05.2009.

- 8:30- 9:10: G. Zwicknagl: “Heavy quasiparticles, instabilities and co-operative phenomena in f-electron systems”
- 9:10- 9:50: P. Hyldgaard: “Van der Waals interactions in sparse matter”
- 9:50- 10:30: M. Alouani: “Tunneling magnetoresistance of Fe/MgO/Fe junctions”
- 10:30-11:00: Coffee
- 11:00-11:40: J. Frantti: “Polarisation rotation in ferroelectrics”
- 11:40- 12:20: L. Nordstroem: “Polarisations of transition metals”
- 12:20-13:30: Lunch
- 13:30-14:10: E.A. Kotomin: “Hybrid functional calculations of point defects in perovskites”
- 14:10-14:50: K. Koepernik: “Recent applications of LSDA+U: An analysis of the method”
- 14:50-15:10: Coffee
- 15:10-15:50: L. Petit: “Large scale predictive calculations of materials properties”
- 15:50-16:30: G.K.H. Madsen: “Electronic-structure theory of thermoelectric materials”
- 16:30-17:10: O. Eriksson: “Data mining electronic structures for new materials”

ABSTRACTS

R.C. Albers

Theory Division, Los Alamos National Laboratorium, Los Alamos, NM (USA).

"DMFT Electronic-Structure Calculations: Fact or Fiction"

In this talk I will present a critical examination of Dynamical Mean-Field Theory (DMFT) calculations as they are implemented in band-structure codes. The critical question is whether the DMFT calculations are really just model-calculations that are pasted on top of conventional band-structures, or whether they have any real electronic-structure significance. For example, how well do they actually integrate with conventional electronic-structure calculations and what are the issues or problems associated with this integration? I will use Pu as my example in these discussions. It is hoped that this talk will provoke much needed discussion to more critically assess how DMFT is used in practice, and how much we can trust the results of these types of calculations.

Tunneling magnetoresistance of Fe/MgO/Fe junctions*

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In this talk, I will discuss the electronic structure and transport properties of Fe/MgO/Fe tunnel junction which were calculated using both the TBLMTO Green's function method and the pseudopotential theory using localized atomic functions and the Landauer formalism [1,2]. These magnetic junctions present a high tunneling magnetoresistance due to spin filtering and the Δ_1 symmetry of the electron tunnel current. The introduction of Cr or V layers, although metallic, affect considerably the transport properties of Fe/Cr(V)/MgO/Fe junctions and play the role of an additional barrier because of the absence of Δ_1 symmetry at the vicinity of the Fermi level. The electronic strucutre characteristics of V and Cr are crucial in the making of Fe/Cr(V)/Fe/MgO/Fe double junctions in order to study resonant electronic transport[3].

*Work in collaboration with S. Sanvito, I. Rungger and S. Lebegue.

1. F. Greullet, C. Tiusan, F. Montaigne, M. Hehn, D. Halley, O. Bengone, M. Bowen, and W. Weber, Phys. Rev. Lett. 99, 187202 (2007).
2. *Structural relaxation effects on interface and transport properties of Fe/MgO(001) tunnel junctions*, Xiaobing Feng, O. Bengone, M. Alouani, S. LebÃ¨gue, I. Rungger, and S. Sanvito, arXiv :0811.1841 (submitted to PRB).
3. *Interface and transport properties of Fe/V/MgO/Fe magnetic tunnelling junctions*, X. Feng, O. Bengone, M. Alouani, I. Rungger and S. Sanvito, PRB (submitted).

Strongly bound electron-hole pairs

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Being intimately related to the probability of radiative emission/absorption and electric-field induced generation of free charge carriers, exciton binding energies are a central quantity in the photophysics of materials used in opto-electronic devices. The binding strength strongly depends on the degree of localization of the involved charge carriers. If the Coulomb interaction is efficiently screened like in tightly packed structures, the electron-hole pairs are nearly free, while strongly bound excitons can be found in low-dimensional and open systems. Hence inorganic semiconductors exhibit typical singlet exciton binding energies of a few meV, while they can be up to 1eV in organic molecular crystals.

From the theoretical point of view excitons can be studied by the solution of the Bethe-Salpeter equation, which provides an effective Schrödinger equation for the electron-hole pair using density functional theory (DFT) as a starting point. Alternatively, one can employ time-dependent DFT (TDDFT), where several exchange-correlation (*xc*) kernels have been proposed in literature, accounting for excitonic effects. We have implementted both, the BSE and TDDFT in full-potential all-electron codes (Wien2k and EXC!TiNG) which not only allow for treating any system irrespective of the atoms involved, but also exploring the core region in terms of electronic excitations.

In this talk, I will give an overview on the scenarios leading to strongly bound excitons, and how the Coulomb interaction can be efficiently suppressed. Here I will mainly concentrate on carbon-based materials, discussing the effect of dimensionality and packing [1-3].

Another focus will be excitonic effects in core level spectra, comparing the BSE results with the popular supercell approach. It will be shown that in case of shallow core states the latter method clearly underestimates the excitonic binding energies [4].

Finally, I will evaluate the performance of different *xc* kernels by comparison of TDDFT results with the solution of the BSE [5].

[1] P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. Lett. 89, 056405 (2002).
[2] K. Hummer, P. Puschnig, and C. Ambrosch-Draxl, Phys. Rev. Lett. 92, 147402 (2004).
[3] K. Hummer and C. Ambrosch-Draxl, Phys. Rev. B 71, 081202(R) (2005).
[4] W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and C. Ambrosch-Draxl, Phys. Rev. B 79, 041102(R) (2009).
[5] S. Sagmeister and C. Ambrosch-Draxl, PCCP, accepted (2009).

pd Wannier functions, bands, and magnetism in FeAs materials

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X-ray magnetic circular dichroism in $CeFe_2$

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The x-ray magnetic circular dichroism (XMCD) spectra of $CeFe_2$ at the Ce $L_{2,3}$, $M_{4,5}$ and Fe K and $L_{2,3}$ edges are investigated theoretically from first principles, using the fully relativistic Dirac LMTO band structure method. The electronic structure is obtained with the local spin-density approximation (LSDA). The origin of the XMCD spectra in the compound is examined. The core-hole effect in the final states has been investigated using a super-cell approximation. It improves the agreement between the theory and the experiment at the Ce M_5 edge, however, has a minor influence on the shape of the Ce $L_{2,3}$ XMCD spectra.

PACS numbers: 75.50.Cc, 71.20.Lp, 71.15.Rf

S. Biermann

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Correlation Effects in Electronic Structure Calculations

We will discuss two examples of materials in which electronic correlations beyond the local density approximation play a role.The first example deals with the new iron oxypnictide superconductors REOFeAs, where we unravel trends for f-electron correlations along the rare earth series. In the second part of the talk we will present dynamical mean field calculations for the optical properties of vanadium dioxide, a material that is of technological interest due to its thermochromic properties.

Data mining and electronic structure theory as a tool in the search for new functional materials

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(Dated: April 28, 2009)

A highly accelerated electronic structure implementation and data mining algorithms have been combined with structural data from the Inorganic Crystal Structure Database to generate materials properties for about 22,000 inorganic compounds. It is shown how data mining algorithms employed on the database can identify new functional materials with desired materials properties, resulting in a prediction of 136 novel materials with potential for use as detector materials for ionizing radiation. The methodology behind the automatized *ab-initio* approach is presented, results are tabulated and a version of the complete database is made available at the internet web site `http://gurka.fysik.uu.se/ESP/` .

Studying the temperature dependence of the electric-field gradient at impurities in oxides using ab initio calculations. Two examples.

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The electronic charge density $\rho(r)$ in a solid and its temperature dependence can be studied by measuring the electric-field gradient tensor (EFG), which is very sensitive to small changes in $\rho(r)$. In this sense, the Perturbed-Angular Correlation technique (PAC) is specially suited to study the temperature dependence of the EFG because its sensitivity is not reduced by temperature effects as in other techniques. In the case of metallic systems, the temperature dependence of the EFG is relatively well understood in the framework of a model that takes into account the influence of lattice vibrations. On the other hand, in the case of semiconducting and insulating systems, several behaviours have been observed, which have been explained (with more or less success) in terms of host properties or processes induced by the presence of the probes (generally impurities in the systems under study).

In the particular case of the wide band-gap semiconductor TiO_2 (rutile structure), the strong dependence of the EFG tensor at Cd impurities with temperature cannot be explained from simple considerations. In order to explain the thermal behaviour of the EFG tensor, the authors of this experiment attributed this dependence to the non-isotropic thermal expansion of the rutile lattice. But they found no means to make a quantitative connection between the two effects [1].

The semiconductors that crystallize in the cubic structure of the mineral bixbyite Mn_2O_3 have been subject of systematic studies with $^{111}In \rightarrow ^{111}Cd$ tracers. In these compounds, the presence of dynamic hyperfine interactions, originated in the electron-capture decay after-effects, and a strong positive linear temperature dependence of the EFG appear selectively, depending on the fact that if the host cations present closed electronic shells (such as Sc, Y, and In) or if it has incomplete electronic shells (as is the case of the 4f-orbitals of the rare-earths). Lutetium is the only rare-earth that presents a closed-shell electronic structure in its 3+ oxidation state, converting this oxide into an interesting "laboratory" to check the models proposed to explain the phenomena mentioned above. The anomalous experimentally observed "step-like" EFG temperature dependence at ^{111}Cd sites in Lu_2O_3 was explained in the framework of a "two-state" model that considers an extremely fast fluctuation between two static EFG configurations, which enabled the experimental determination of an acceptor energy level introduced by the Cd impurity in the band-gap of the semiconductor and the estimation of the oxygen vacancy density in the sample [2].

In this talk we show how a "0K" *ab initio* calculation can explain the temperature dependence of the EFG at Cd impurities in TiO_2 and Lu_2O_3. Calculations were performed with the Full-Potential Linearized-Augmented Plane Waves (FP-LAPW) method.

In the first example (Cd-doped TiO_2), some years ago we have shown that at 300 K the Cd impurities introduce strong lattice distortions in the TiO_2 lattice [3]. Now, for a given temperature, we calculate (using the thermal expansion coefficients) the corresponding lattice parameters. These lattice parameters are used in the FP-LAPW calculations. For each set of lattice parameters (that correspond to a given temperature), we obtain the new structural distortions introduced by the Cd impurities and the resulting EFG tensor. We found that the structural distortions depend on the temperature considered and are at the origin of the strong temperature dependence of the EFG tensor.

In the case of Cd-doped Lu_2O_3, the temperature dependence of the EFG can be understand from the ionization of an impurity single acceptor level introduced in the band-gap of the semiconductor by the Cd impurity [4].

Both examples show the capability of *ab initio* calculations to complement hyperfine experiments also at varying temperatures.

[1] J. C. Adams and G. L. Catchen, Phys. Rev. B 50 (1994) 1264.
[2] LA.Errico, M. Rentería, A.G.Bibiloni, and F.G.Requejo, Hyperfine Interact.120-21, 457 (1999).
[3] L. A. Errico, G. Fabricius, M. Rentería, P. de la Presa, and M. Forker, Phys. Rev. Lett. 89 (2002) 55503.
[4] L.A. Errico, M. Rentería, A. G. Bibiloni, and G. N. Darriba, Physica Stat. Solidi C 2, 3576 (2005).

Electromechanical response in ferroelectric perovskites in the vicinity of the morphotropic phase boundary

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The origin of the very large piezoelectric response observed in the vicinity of the morphotropic phase boundary (MPB) in perovskite lead zirconate titanate (PZT), and related systems, has been under intensive study. Though there is a consensus that the vicinity of the phase boundary has a crucial role for the enhanced piezoelectric properties, keen efforts have been dedicated to understand the microscopic origin of the electromechanical response in these systems. Polarization rotation ideas are frequently invoked to explain the piezoelectric properties, and a close connection is made to the monoclinic symmetry. A classical example is provided by the PZT system, in which the monoclinic Cm phase is often stated to serve as a bridge between the rhombohedral and tetragonal phases. We demonstrate that the polarization rotation model does not provide an explanation for the enhanced electromechanical properties. Notes on more general grounds are given to demonstrate that a continuous phase transition between the rhombohedral and tetragonal phases via an intermediate monoclinic phase is not possible and correspondingly the slight deviation of the spontaneous polarization direction from the tetragonal c-axis direction (for instance, the Cm symmetry observed in PZT) in the vicinity of the phase boundary has no central role. Instead, two-phase coexistence in the vicinity of the phase transition region has an important role as regards electromechanical properties.

The next task is to consider the necessary requirements for the MPB. High-pressure study of lead titanate ($PbTiO_3$, PT) provides a platform, which is free from the difficulties related to the solid solutions, to tackle the phase transition behavior in piezoelectric perovskites. We show, through high-pressure (up to 8 GPa) neutron powder diffraction experiments and density-functional theory computations on PT that it is the competition between two factors which determines the MPB. The first is the oxygen octahedral tilting giving advantage for the rhombohedral $R3c$ phase, and the second is the entropy, which in the vicinity of the MPB favours tetragonal phase above 130 K. If the two factors are in balance over a large temperature range, a steep phase boundary results in in the pressure-temperature plane.

Understanding correlations in vanadium dioxide from first principles

Matteo Gatti*,[1,2,3] Fabien Bruneval,[1,4] Valerio Olevano,[1,5]
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Vanadium dioxide (VO_2) is a prototype material for the discussion of correlation effects in solids. Here we present a parameter-free GW calculation of VO_2 and show that correlation effects in the photoemission spectra of both the metallic and the insulating phases of VO_2 are correctly reproduced, provided that quasiparticle energies and wavefunctions are calculated self-consistently [1]. Moreover, our calculations explain the satellite in the photoemission spectrum of the metal as due to a plasmon resonance in the energy-loss function and show that this feature disappears in the insulator.

These ab initio calculations are computationally demanding and one is naturally led to search for possible alternatives. In fact, spectra are theoretically derived from contractions of many-body Green's functions. So one calculates more information than needed. We hence illustrate an in principle exact alternative approach to construct effective potentials and kernels for the direct calculation of electronic spectra [2]. In particular, a dynamical but local and real potential yields the spectral function needed to describe photoemission. Finally, we discuss for model solids the frequency dependence of this "photoemission potential" stemming from the nonlocality of the corresponding self-energy.

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[1] M. Gatti, F. Bruneval, V. Olevano, and L. Reining, Phys. Rev. Lett. **99**, 266402 (2007).
[2] M. Gatti, V. Olevano, L. Reining, and I.V. Tokatly, Phys. Rev. Lett. **99**, 057401 (2007).

Calculations of the band structure of In-containing nitride alloys

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Abstract

In-containing nitide alloys: InGaN, InAlN and InGaAlN have been recently of major interest due to their applications in optoelectronics for the construction of green-blue-violet light emitters. Effect of indium clustering, which is believed to be crucial for efficient radiative recombination, its possible influence on the band structure of In-containing alloys, as well as experimental data showing significant bowings of Eg and dE_g/dp motivated the present work. We analyzed the band gaps and its pressure coefficients variation with indium concentration in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ for a wide range of x. Some preliminary calculations were performed for quaternary alloy $In_xGa_{1-y}Al_{1-x-y}N$.

Approach based on the Local Density Approximation (LDA) to density functional theory, with the Perdew-Zunger parametrization of the Ceperley-Alder exchange-correlation was used. The calculations were performed in two step, applying two computational schemes. The first one, pseudopotentials as implemented in the Vienna *Ab-initio* Simulation Package (VASP), was used for calculations of the atomic relaxations in the entire supercell by minimizing the Hellman-Feynman forces. Band structures of the alloys were obtained in the second step by the Full-Potential Linear-Muffin-Tin-Orbital method. To correct for the LDA band-gap errors a semiempirical correction scheme was applied.

We simulated the effects of In segregation by different distributions of In atoms in the 32-atom supercell. It was found that both, the band gaps and its pressure coefficients, exhibit large bowings, in particular when In atoms are ‘clustered’.

Looking for the possible explanation of the observed anomalies in the Eg and dEg/dp behavior we make detailed analysis of the valence band density of states. The unusual decrease in both the band gaps and their pressure coefficients with In content seems to come from the In-induced changes of the states at the valence band top. It relates to the increase of the valence band width due to (hybridization) admixture of In *p* and *d* states into the uppermost N_p valence states. As results from the detailed analysis of the lattice relaxation strong interaction of In and N is related to significantly shorter bonds between them in the clustered case in comparison with uniformly In-distributed case.

Ab-initio theory of superconductivity

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Electron-phonon coupling in correlated systems

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The electron-phonon interaction (EPI) is discussed for strongly correlated systems. For non-interacting electrons, effects of the EPI can often be characterized by the coupling strength and the phonon frequency. For strongly correlated systems this information is not sufficient. It is argued that effects of the EPI depends crucially on which phonons are considered and which property is studied. These issues are discussed, using examples from alkali-doped fullerides and high-T_c cuprates.

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Importance of bulk reduction for molecular reactions at rutile TiO2(110) surfaces

I present a combined DFT and STM study of the interaction of water and oxygen molecules with the rutile TiO2(110) surface [1-7]. With the STM, some elementary reaction steps of the water and oxygen are imaged. Water molecules are found to diffuse[2] and form dimers on these surfaces[7].

When diffusing near bridging oxygen vacancies on the surface, the water may dissociate in these vacancies[2]. Water is further found to mediate the diffusion of bridging hydroxyl groups resulting from the dissociation proess[2]. Molecular oxygen is found to react via two competing pathways: i) dissociation in bridging oxygen vacancies and ii) dissociation in the Ti troughs. The former results in a healed bridging oxygen vacancy and one oxygen adatom in the Ti trough [1], while the latter leads to two oxygen adatoms in the trough [4]. Molecular oxygen is further found to be able to oxidize hydrated rutile TiO2(110) surfaces through a process in which the adsorbed oxygen picks up protons from the surface and eventually reduces to adsorbed water[6]. All the above situations are modeled with DFT where small barriers and favorable reaction energetics are found only if the TiO2 crystals are modeled in a reduced state. This may be done in several ways, e.g. by inclusion of bulk oxygen vacancies [1] or bulk Ti interstitials [4]. In the STM investigations, new island-like structures appear on the surfaces upon warming to temperatures below the O2 TPD peak (i.e. below 410 K). By comparison to DFT results these structures are interpreted as resulting from the interaction between bulk Ti interstitials and oxygen chemisorbed at the surface [4]. Finally, the results are discussed in the context of the general use of TiO2 as a support material for gold nanocluster catalysts [3,5].

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van der Waals interactions in sparse matter

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Sparse matter contains important regions with low concentration of electrons where dispersive or van der Waals (vdW) interactions contribute to the materials binding and behavior. The class of sparse matter is broad as it contains layered materials, polymer and molecular systems as well as many surface and interface systems. The internal voids in the electron density permit a large flexibility in the local morphology and a possibility of subtle variations in the binding of material and/or molecular fragments. Nature exploits sparse-matter interactions in molecular recognition to carefully control assembly of biomolecules that regulate life processes and there are both fundamental and technological reasons to seek an improved understanding of electron behavior in sparse matter.

Sparse matter represents challenges for quantum-physical calculations because we must simultaneously account for the traditional types of bonding (for example, within a molecule or within a graphite sheet) and the interactions (for example, between molecules or between the sheets) mediated across the internal voids. Generally, dispersive interactions exist in concert with traditional bonds. Simply adding an asymptotic vdW description is inconsistent with both saturation and multipole effects that dramatically enhance the vdW strength at relevant binding separations. Traditional formulations of density functional theory (DFT) rest on local and semi-local functionals and fail to describe sparse matter because they do not include the nonlocal correlations provided by the electron coupling to the electrodynamic field.

My talk will summarize our Chalmers and Rutgers work to formulate a van der Waals density functional (vdW-DF) that includes nonlocal correlations and dispersive interactions without double counting and which provides a transferable account of sparse (soft) and dense (hard) materials. My talk also describes our vdW-DF calculations of molecular interactions: (1) benzene on Cu(111) as a model system for acene self-assembly in a system where vdW binding competes with a surface-state mediated indirect electronic interaction and (2) nature of binding in crystals of platonic and platonic-like molecules.

Recent applications of LSDA+U: an analysis of the method

Klaus Koepernik

Abstract

The local spin density approximation + onsite Coulomb repulsion approach (LSDA+U) is a widely used approximation to incorporate effects of strong electron correlation into the frame work of density functional theory. The method can be applied successfully in the limit of strongly localized d- and f-shells. However, the method has two unknown ingredients, the value of U and the form of the double counting term. While several ways to calculate U have been devised in the recent years, a clear understanding of the proper usage of the existing double counting terms seems to be missing. We analyze various effects of the "$+U$" part of the functional. Besides the penalty for double occupation, the self-interaction and the isotropic and anisotropic exchange are discussed. The example of a model $4f$-shell is used to obtain further insights into the performance of the different flavors of the double counting term, used in the literature. Recent results for the high-spin to low-spin transition under pressure of MnO and CoO, obtained via LSDA+U, are discussed to illustrate the analysis of the energetics.

Hybrid functional calculations of point defects in ABO_3 perovskites

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ABO_3 compounds comprise a rich family of crystalline structures: simple cubic (Fig.1), tetragonal, orthorhombic, *etc.* which corresponds to the ferroelectric, antiferroelectric, and other phases with specific technologically important properties. In spite of substantial efforts, the nature of defects in ABO_3 perovskites is still poorly studied. One of the main and the most important defects is an *oxygen vacancy* with trapped electrons called the *F* center. Detailed analysis of *F* center calculations in perovskites for both bulk and densely packed surfaces is summarized in our previous articles [1-3].

We present a *comparative study* of the *F* centers in three important perovskites: $SrTiO_3$ (widely used as a substrate for growth of high-T_c superconductors), $PbTiO_3$ (actuators and sonar devices) and $PbZrO_3$ (diagnostic material for radiation environment). We analyze how variation in A (Pb or Sr) and B (Ti or Zr) cations changes properties of pure materials and defects therein. First principles periodic defect calculations have been performed using the *CRYSTAL-06* code based on the basis of atomic orbitals (LCAO) combined with the DFT-HF (B3PW) non-local hybrid exchange-correlation functionals. When modelling defects, a simple cubic (high-temperature) unit cell containing one formula unit (5 atoms) was extended to a n×n×n supercell (Fig. 1). Our calculations for orthorhombic $PbZrO_3$ [3] do not show substantial difference with the cubic phase for a defect structure, this is why we mainly considered noticeably simpler cubic phase.

Different nature of chemical bonding in Pb- and Sr- as well as Ti- and Zr-containing perovskites (partial Pb-O bond covalency *vs.* almost nominal ionic charge for Sr^{2+} as well as larger ionicity of Zr as compared to Ti atoms) results in a noticeable difference in the character of relaxation around point defects and other properties.

One of the main defect characteristics is the energy level position with respect to the energy bands of a pure material which controls both electron/hole localization and defect stability. The calculated band structures for the cubic $PbTiO_3$, $PbZrO_3$, and $SrTiO_3$ containing *F* centers show difference between the *F* centers. In $PbZrO_3$ this is a deep defect, with the donor level close to the middle of the gap, 1.7 eV below the bottom of conduction band (CB). The defect energy band caused by the interaction of periodically repeated defects has a small dispersion over the Brillouin zone (0.14 eV). In contrast, in $PbTiO_3$ and $SrTiO_3$ titanates, the defect level is much closer to CB bottom, characterized by a larger dispersion. In other words, these are shallow defects unstable at moderate or high temperatures. As to defect formation energy, it is noticeably larger for STO than for PZ and PTO.

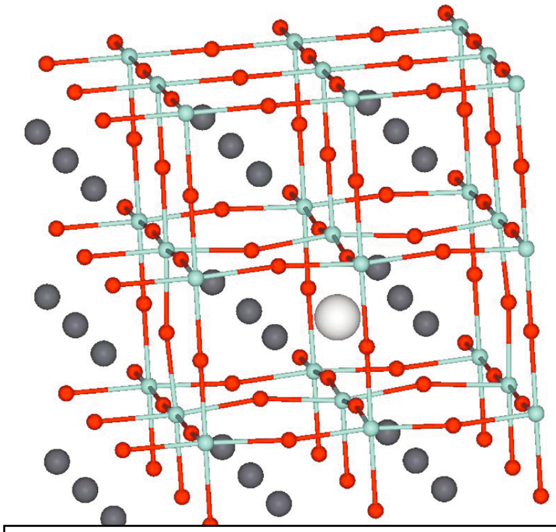

Fig. 1. 3×3×3 supercell of ABO_3 crystal containing an O vacancy shown as the largest light gray ball.

The F centers on the (001) surfaces are typically more shallow and delocalized than in the bulk. We predict considerable defect segregation from the bulk to the surface.

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ELECTRONIC, MAGNETIC, AND TRANSPORT PROPERTIES AND MAGNETIC PHASE TRANSITION IN QUATERNARY (Cu,Ni)MnSb HEUSLER ALLOYS

The electronic properties, finite-temperature magnetism, and transport properties of semi-Heusler quaternary alloys (Cu,Ni)MnSb are studied theoretically by means of *ab initio* calculations as a function of the alloy composition. As documented by experiment the transition from the ferromagnetic state (NiMnSb) to the antiferromagnetic state (CuMnSb) gives rise to an abrupt change of the magnetic moments and resistivities at about $x_{\mathrm{Cu}} \approx 0.7$ while the Curie temperature exhibits a smooth behavior with the Cu-content. We explain this peculiar behavior with the onset of disorder in orientations of the Mn-spins at $x_{\mathrm{Cu}} \approx 0.7$. A simple account of magnetic disorder based on the so-called uncompensated disordered local moment picture provides a good quantitative understanding of available experimental data. An origin of the observed magnetic phase transition is also discussed.

(*) In collaboration with Václav Drchal and Ilja Turek

Electronic structure, magnetism and phonons in rare-earth nitrides, Gd-pnictides and Eu-chalcogenides

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January 12, 2009

Abstract

The rare-earth nitrides provide an interesting testing ground for electronic structure theories of strongly correlated electrons. In spite of their common simple rocksalt structure, the properties of the rare-earth nitrides and related compounds show significant variation because of the partially filled 4f shell. In recent years, there have been renewed efforts to grow these materials stoichiometrically pure and this opens the way to a better understanding of their basic properties. We have used LSDA+U (local spin density functional theory with Hubbard U corrections) to study these compounds and have closely collaborated with experimentalists to carrying out various spectroscopic studies of these materials. I will first present an overview of their trends in electronic structure, emphasizing some symmetry aspects of LSDA+U. We find in particular, that Hund's rules are obeyed in most of these compounds and constitute a symmetry breaking because of the rule of maximum L_z in the ferromagnetic configuration.[1] We made an in-depth study of the magnetic exchange interactions in Gd pnictides (GdP,GdAs, GdSAb, GdBi) as well as Eu-chalcogenies, explaining the trend in their Néel temperatures.[2, 3, 4] The same theoretical model however, shows GdN, which is semiconducting instead of semimetallic, to be ferromagnetic. This ferromagnetism is shown to correspond to a perfect antiferromagnetic arrangement of the opposite moments induced on the Gd-d and N. We show consistency between the predictions of full-potential linearized muffin-tin orbital band calculations and linear response atomic sphere approximation calculations even though the underlying analysis of the exchange interactions is somewhat different. Interestingly, the predicted Curie temperarure of GdN is significantly underestimated, even though our Néel temperatures for the other pnictides are in good agreement with experiment and even for metallic Gd, we obtain reasonable estimates of the Curie temperature. This indicates that experimental Curie temperartures may be influenced by defects, such as nitrogen vacancies. We present a detailed study of the interband transitions in GdN [5] and discuss experimental evidence for the semiconducting character of GdN even below the Curie temperature[7] and the red-shift of the gap upon magnetic ordering. We present also the results of X-ray emission and absorption studies and their comparison with theory.[6] Finally, we discuss the Raman spectra observed in rare-earth nitrides.[8] These are shown to be disorder induced first-order Raman spectra exhibiting a density of states like spectrum, strong weighting the zone boundary modes at the L-points. We show the resemblance of these spectra to those in ScN [9] and discuss the trend in phonon frequencies.

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BSE and LDA+U calculations for delafossites and ZnO

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We report on the calculations of optical properties of ZnO and $CuAlO_2$ where we combine LDA/GGA+U method with the solution of the Bethe-Salpeter equation (BSE) in order to include the electron hole correlations. For the both compounds the DFT band structure shows the d-shell lying too close the Fermi level. This affects the hybridization with the metal s bands resulting in the slightly wrong charge distribution at the atomic site affecting calculated electric field gradients (EFG), and also the distribution of the energy levels at the band gap. Applying the LDA/GGA+U method with the large U (8-12 eV) for the full d shells of Zn and Cu we are able to shift them from the Fermi level in the experimentally determined position. We show that this procedure improves calculated EFG, optical spectra as well as the distribution of the energy levels around the band gap.

The Flavours of SIC

Martin Lüders, Daresbury Laboratory

Since its introduction by Perdew and Zunger, there have been several different implementations of the self-interaction corrected (SIC) local (spin) density approximation, in particular when applied to extended systems. In this talk, I will give a short overview of these approaches and discuss how they relate to each other and their major differences. In particular, I will focus on the (full) SIC, implemented in the LMTO code, on the local SIC, implemented in multiple scattering theory, and on the so-called pseudo-SIC. I will also comment on their intended fields of application and show some results, comparing the methods, where applicable.

Electronic-structure theory of thermoelectric materials

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(Dated: March 30, 2009)

Thermoelectric materials have applications in both Peltier-cooling and in converting waste heat to electrical energy. Due to the discovery of new materials the area has received much attention the past decade.

The search for new thermoelectric materials is a quest to maximize the dimensionless figure of merit $zT = (\sigma T/\kappa)S^2$, where S is the Seebeck coefficient and σ and κ are the electronic and thermal conductivities respectively. zT quantifies the performance of a thermoelectric and one must therefore maximize the power factor $S^2\sigma$ and minimize κ. S, σ and κ are coupled and all depend strongly on the detailed electronic structure, carrier concentration and crystal structure, which makes the task of finding new compounds with large values of zT extremely difficult.

Based on a case study of $CsBi_4Te_6$ I will show how electronic structure calculations can be used to rationalize the behavior of known materials. In this process some fingerprints, which characterize good performance, are identifies. These observations are used to construct a screening of the inorganic crystal structure database for potential thermoelectric materials. I will show how this resulted in the discovery of two new materials: $FeSb_2$ and LiZnSb.

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Ab-initio calculations of *FCC*-FeMn alloys with the $L1_0$ crystallographic structure

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The antiferromagnetic *FCC*-phase of FeMn alloys has been the subject of numerous studies over recent decades [1-2]. Three magnetic structures, 1*Q*, 2*Q* and 3*Q*, based on the position and orientation of spins [1], have been proposed and studied. However, despite all the efforts of several theoretical and experimental works to determine unambiguously which one corresponds to the ground state, or at least to exclude some of them. These results always came up to contradictory conclusions, or confusing results, depending on the resolution of the experimental technique used [1, 3-4]. That is why there were attempts to resolve the problem through *ab-initio* calculations using the crystallographic structure $L1_0$ [5-7]. These calculations appear to overturn the balance in favor of the 3*Q* structure, however, this structure does not represent a completely random alloy, as is the case. Regarding that, the results of several variations of possible antiferromagnetic spins directions in the FeMn $L1_0$ structure are presented as a first step of calculations to the more complicated structure B21, which is closer to a random alloy. The calculations were performed with a full-potential linearized augmented-plane-wave code and the results obtained, with several types of exchange and correlation functional, were compared with reported experimental data.

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Polarisations of transition metals

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(Dated: February 22, 2009)

For transition metal systems the concept of polarisation of the open shell plays a vital role. The most significant is of course spin polarisation. Well known are also the orbital orderings occurring in e.g. oxides and the orbital moment formations in e.g. rare earths. Recently, we have generalised the concept of polarisation by an exact spherical tensor decomposition of the exchange energy[1]. In the current presentation we will primarily focus on different polarisation channels of actinide systems where spin orbit coupling plays a crucial part.

The magnetism involving the $5f$ states of the actinides show many exotic behaviours. One of the most dramatic examples is the tiny magnetic moments[2] observed in e.g. tetragonal $\mathrm{URu_2Si_2}$ at low temperatures. It is established that the true order parameter driving this second order transition is hidden, i.e. not observable by standard techniques. Many hypotheses for this "hidden order" (HO) have been suggested, ranging from quadrupoles through spin nematics to orbital currents, but have all found to be inconsistent with experimental findings.

Here we find, by electronic structure calculations combined with a tensor moment analysis, that a non-trivial magnetic triakontadipole (rank five) moment plays an important role in magnetically ordered materials with a large effective spin-orbit coupling in general, and that it is "the" order parameter in $\mathrm{URu_2Si_2}$. Our calculations which treat the $5f$ states as itinerant with large Coulomb interaction shows that what makes some heavy fermion systems such as $\mathrm{URu_2Si_2}$ unique is that in the presence of the large triakontadipole moment, both the spin and orbital dipole moments become very small. In order to stabilize these pure anti-ferromagnetically ordered multi-pole moments in $\mathrm{URu_2Si_2}$ it is found theat the Fermi surface nesting is essential in accordance with other recent studies[3]. In $\mathrm{URu_2Si_2}$ under pressure, which corresponds to decreased in-plane lattice constant, the dipoles increase giving rise to ordinary magnetic moments in accordance with experiments[4], while the magnetic multi-pole decreases slightly.

The presence of this magnetic multi-poles in our calculations points to the need of a re-evaluation of our understanding of polarisation and magnetic order in the presence of strong effective spin-orbit coupling. As a first step in this direction we propose a complementary set of rules, the Katt's rules, as an alternative to Hund's rules[5] in this limit. We will describe the analysis which leads, counter-inuitively, to the important role played by these high rank tensors in the case of heavy magnetic elements.

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Electronic structure of URu_2Si_2 and of correlated Pu-materials*

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The hidden order (HO) in the heavy-fermion superconductor URu_2Si_2 has been studied for more than 20 years; however, the origin of this unusual phase has remained a mystery. We present here a microscopic explanation for the HO. We demonstrate [1] that density-functional theory-based electronic structure calculations explain very well *all* the known properties of the paramagnetic and large moment antiferromagnetic (LMAF) phases. Exploiting the known experimental equivalence between the Fermi surface properties of the LMAF and HO phases, we identify the Fermi surface hot spots where a Fermi surface instability is lifted through spontaneous symmetry breaking. We quantify that symmetry breaking through a collective mode of longitudinal, antiferromagnetic fluctuations does induce a substantial Fermi surface gapping and thereby drives the transition to the HO phase. Our explanation consistently explains the transport properties as well as entropy loss of the HO phase [1].

We furthermore present electronic structure results on various correlated Pu-compounds, which we recently computed.

*Work done in collaboration with S. Elgazzar, J. Rusz, M.-T. Suzuki, J.A. Mydosh & Y. Yun.

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Electronic Phase Diagram of Rare Earth Materials.

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Abstract

We investigate the potential of high throughput computing for predicting new materials from a systematic study of the groundstate properties of whole compound families. The self-interaction corrected local spin density (SIC-LSD) approximation is used to predict the ground state valency configuration of the manifold of rare earth mono-pnictides and mono-chalcogenides. For a given compound, the ground state is determined by minimizing the SIC-LSD total energy functional, modified to account for multiplet formation energies (tetrad effect). This minimization process requires some 40 self-consistent runs per system, with 140 compounds being investigated, and the corresponding calculations have been run using the NW-GRID (UK's North-West facility). The resulting electronic phase diagram of the rare earth pnictides/chalcogenides is characterized by valency transitions brought about by a complex interplay of ligand chemistry on one hand, and lanthanide contraction on the other hand. The predicted groundstates, from the trivalent "early" pnictides to the divalent "late" chalcogenides, are in good agreement with experiment.

Impurity vibration modes in semiconductors

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Ab initio simulations of crystal vibrations are by now routinely done for perfect periodic pure systems, either by the linear response or by the frozen phonons technique. The domain of substitutional alloys even in its simplest limiting case, that of a single impurity, is technically demanding because of the necessity to take into account the local, translation-breaking elements (difference in the substituted mass; disorder of coupling constants) along with the essentially delocalized ones (connectivity of different chemical bonds, long-ranged interactions contributing to interatomic force constants). This duality makes the phonons a very specific type of probe for the elastic properties in a mixed crystal; namely, a probe at the mesoscopic level.

In order to reveal the elastic information behind the observed vibrational properties, accurate *ab initio* calculations in combination with clear-cut and representative structure models are of primary importance [1]. Speaking specifically of II-VI and III-V semiconductors, a single isovalent substitution (on either cationic or anionic sublattice) would be such clear-cut model case, whereas a subsequent inclusion of the second impurity of the same kind would imitate a germ of the solid solution. It turns out indeed that the vibration spectra in II-VI or III-V pseudobinary semiconductor alloys (A,B)C are largely shaped by the vibration properties of pure parent compounds AC, BC and by the impurity vibration modes AC:B, BC:A, as the obvious limiting cases. A generally complicated behavior in the intermediate range of concentrations may be to some extent grasped from the analysis of how do the impurity modes split due to their interaction, just away from the dilution limit. Serving as a parameter gained primarily from *ab initio* calculations (and verified in experiment whenever possible), this splitting helps to describe the vibration modes in the whole concentration domain, making use of the so-called percolation model [2]. This approach offers a unified view at the phonon behaviour in large number of pseudobinary systems characterized by very different levels of contrast between masses and elastic properties of parent compounds, and overcomes the limitations of the too simplistic virtual crystal approximation (or similar) model.

The richness of the two-impurity case is based on the fact that several tendencies are in play (symmetry constraints; loss of isotropy in the lattice relaxation in the vicinity of a defect), which are manifested differently in different alloys, depending on their chemistry and elastic contrast. The examples of such diversity will be given, for a number of zincblende- and wurtzite-type mixed semiconductors. Technically, calculations are done by the Siesta method, applying the finite-displacement technique to scan all force constants in sufficiently large (64 atoms in zincblende, 96 in wurtzite) supercells.

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APW+lo and TDPAC Study of the Electric-Field Gradients at the Cation Sites of the ^{44}Ti(EC)^{44}Sc -doped Semiconductor Sc_2O_3

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We report on an *ab initio* study of the electric-field-gradient tensor (EFG) at both inequivalent Sc sites in the semiconductor Sc_2O_3. Calculations were performed with the Full-Potential Augmented-Plane Waves plus Local Orbitals (FP-APW+lo) method that allows us to treat the electronic structure and the atomic position refinements in a fully self-consistent way. Our results are compared with recent experimental data determined by Time-Differential γ-γ Perturbed-Angular Correlation (TDPAC) spectroscopy using the first excited I=1 state of the ^{44}Ti(EC)^{44}Sc isotope. It is clear from our results that simple models such as the Point Charge Model can not even approximately describe the measured EFGs at cation sites in pure scandium sesquioxide .

Electronic Structure of the Perovskite Oxide Interfaces: Perspectives and New Physics

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The recent landmark demonstration of the growth of high-quality, lattice-matched perovskite oxide interfaces, e.g., $LaAlO_3/SrTiO_3$, $LaTiO_3/SrTiO_3$, and $CaRuO_3/CaMnO_3$ interfaces, has led to a flurry of activities in this area, leading to the hope of using these structures for new fundamental science as well as for novel applications. These materials are d electron systems with competing interactions such as strong electron correlation, Jahn-Teller coupling to lattice, intermixing between the spin and orbital degrees of freedom, etc., which lead to novel correlated-electron physics, different from the standard semiconductor physics; hence the possibility of paradigm shift in new device applications. For instance, in the LAO/STO interface, a variety of electronic behavior such as Kondo resistance minimum, magnetism, superconductivity, two-dimensional electron gas, etc., have been observed. I will discuss a number of experimental results on these interfaces and the understanding obtained from our recent density-functional and model theoretical studies on these systems.

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Electronic Structure and Exchange Interactions in Superconducting Pnictides

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By using first-principles density functional theory calculations combined with tight-binding method, dynamical mean field theory, and linear response theory, we investigated the electronic structures and magnetic interactions of the nine ferropnictides representing three different structural classes. Proposed tight-binding parametrizations provide a clear picture for the general electronic structure. The calculated magnetic interactions are found to be short-range, and the nearest (J_1) and next-nearest (J_2) exchange constants follow the universal trend of $J_1/2J_2 \sim 1$, despite of their extreme sensitivity to the z-position of As. This suggests the magnetic frustrations as the key factor for stabilizing the superconducting ground state. The calculated spin wave dispersions show strong magnetic anisotropy in the Fe plane, in contrast to cuprates.

Magnetic exchange interactions in the Quasiparticle Self-Consistent GW approximation.

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The quasiparticle self-consistent GW (QSGW) approximation is a means for producing the (near) optimum one-body hamiltonian for the electronic structure of solids. It is useful in its own right as a high-quality one-body hamiltonian, e.g. to describe energy bands, optical properties or transport in an indepedent-particle framework, or as a starting point for many-body calculations.

We present some applications of QSGW in the first context for some representative compounds taken throughout the periodic table. We show that this scheme offers a realistic path for true ab initio device design. While the theory is generally very successful, some systematic errors emerge. The main portion of these errors can be explained in terms of electron-hole interactions missing in the RPA approximation to the dielectric function, though vertex corrections must also play a role in some cases.

In the latter context, we calculate the dynamical transverse spin susceptibility. This enables us to investigate spin wave and Stoner excitations, either within the time-dependent local-density approximation, or starting from the QSGW one-body hamiltonian. Modest changes are found for elemental metals such as Fe or Co, but the differences become dramatic in compounds such as MnAs and NiO. A different picture of spin waves in the DMS compound GaMnAs also emerges: exchange interactions are found to be rather shorter ranged than predicted by the LDA. If time permits, we will show some new results for the iron pnictide CaFeAs.

Actinides: Total energy and GW calculations.

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Total energy calculations are performed for actinide compounds using the self-interaction corrected (SIC) local-spin-density approximation. The total energy minimum leads to the expected trivalent (tetravalent) actinide configuration for the sesqioxides A_2O_3 (dioxides AO_2). In contrast, for the monocarbides and mononitrides, SIC finds a more complex picture with coexisting localized and band-like f-states. In this way the formalism allows an interpolation between the fully itinerant behavior of the f-electrons, valid for UC, and the fully localized behavior encountered for AmN, CmN and CmC.

The quasiparticle self-consistent GW (QSGW) method is applied to elemental U, Np and Pu in their fcc and bcc phases, as well as to the dioxides of U, Np, Pu, and Am. For the elements we find a significant reduction of the band width and crystal field splittings of the f-bands compared to the LDA. For the dioxides the QSGW leads to separated lower and upper Hubbard bands and insulating ground states. In contrast to SIC and LDA+U, the QSGW method predicts in a parameter-free way the position of the f-manifold with respect to the non-f valence bands.

In collaboration with: L. Petit and N. E. Christensen (Århus, DK), Z. Szotek and W. M. Temmerman (Daresbury, UK), A. N. Chantis and R. C. Albers, (Los Alamos, NM, USA), M. van Schilfgaarde, (Tempe, AZ, USA), T. Kotani, (Tottori, Japan), G. M. Stocks, (Oak Ridge, TE, USA).

Structural phase transitions and fundamental band gaps of $Mg_xZn_{1-x}O$ alloys from first principles

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The structural phase transitions and the fundamental band gaps of $Mg_xZn_{1-x}O$ alloys are investigated by detailed first-principles calculations in the entire range of Mg concentrations x, applying a multiple-scattering theoretical approach (Korringa-Kohn-Rostoker method). Disordered alloys are treated within the coherent potential approximation (CPA). The calculations for various crystal phases have given rise to a phase diagram in good agreement with experiments and other theoretical approaches. The phase transition from the wurtzite to the rock-salt structure is predicted at the Mg concentration of $x = 0.33$, which is close to the experimental value of $0.33 - 0.40$. The fundamental band gap, typically underestimated by the local density approximation, is considerably improved by the self-interaction correction. The increase of the gap upon alloying ZnO with Mg corroborates experimental trends. Our findings are relevant for applications in optical, electrical, and in particular in magnetoelectric devices.

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Ab initio study of vacancies in cubic zirconia.

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Zirconia-based materials are in the focus of interest for many years because of their outstanding electrical and mechanical properties. In various forms and with the addition of small amounts of impurities, it has applications ranging from solid oxide fuel cell electrolytes to catalyst substrates, and protective coatings. They also show a rich variety of crystal structures depending on pressure, temperature, impurity/dopant content, growth conditions, etc.

ZrO2 has three polymorphs at atmospheric pressure: the low-temperature phase is monoclinic, and is transformed to a tetragonal phase, and finally to a cubic phase as temperature increases. I well know that high defect concentration stabilizes the cubic fluorite-type polymorph of zirconia with respect to the tetragonal and monoclinic phases. Cation-doped zirconia ZrO2 with aliovalent cations such as Y, Ca, Sc, etc., is known to increase the number of oxygen vacancies which in turn facilitates anion conductivity.

We have performed an ab initio density functional theory study of oxygen vacancies in cubic ZrO2. The equilibrium configuration the and electronic structure of neutral and charged vacancies were calculated for two vacancies concentrations (2% and 0.5%). In all cases we determined the electric field gradient tensor (EFG) at the Zr-nucleus. From these results, we can obtain the EFG distribution for each vacancy concentration and charge states. This distribution can be compared with experimental results obtained in Perturbed Angular Correlation experiments.

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Disordered Local Moment Description of Magnetism in 3d-monoxides and heavy 4fs.

Walter Temmerman, Daresbury Laboratory

We combine the local-self interaction correction (L-SIC) LSD: parameter-free theory, which describes the electronic and magnetic properties of the strongly correlated systems, with the disordered local moment (DLM) theory to provide a finite T description of magnetism, in an ab initio manner, in correlated electron systems. We apply this new methodology to the study of magnetism in MnO, FeO, CoO, NiO and the nature of the magnetic state above the Néel temperature.[1] We also study the magnetic structure in the heavy rare earths and the relationship to the lanthanide contraction.[2,3]

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Work done in collaboration with: Ian Hughes, Julie Staunton (Warwick), Dzidka Szotek, Martin Lueders (Daresbury), Markus Daene, Arthur Ernst, Wolfram Hergert (Halle), Julian Poulter (Bangkok), Leon Petit, Axel Svane (Aarhus), Balazs Gyorffy (Bristol) and P. Strange (Kent).

Heavy quasiparticles, instabilities and co-operative phenomena in f-electron systems

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f-electron systems exhibit highly complex phase diagrams with a multitude of competing phases. Of particular interest is the correlated heavy Fermi liquid state and its instabilities. In this talk I will present results of the Renormalized Band Theory and mucroscopic model calculations using examples from lanthanide and actinide compounds.

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