Ψ_k Newsletter

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

Number 56 April 2003

Editor: Z. (Dzidka) Szotek
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Contents

1 Editorial

In this Newsletter we have several workshop/school/conference/meeting announcements, spread over four sections: **RTN1**, **ESF**, **CCP9**, and **General Announcements**. In particular, we would like to turn readers attention to the final announcement of the **"B. L. Györffy Event"** in Bristol, which is a conference organized on April 11-12, 2003, to celebrate Balazs' contributions to theories of the electronic structure of solids. The title of the conference is **"Order and disorder in solids: alloys, magnetism, and superconductivity"**. In the **ESF section** we also have a report on a meeting of Work Group 15, "Ab-initio design of structural materials", of the new ESF Programme. Abstracts of contributed papers of this meeting are included. More abstracts of newly submitted papers can be found in the usual **Abstracts section**, which follows the **General Job Announcements section**. In the section **Presenting Other Initiatives** an information on new release of the **PWscf package** can be found. The scientific highlight of the month is by Karsten Held (*MPI Stuttgart*), I.A. Nekrasov (*Yekaterinburg*), G. Keller (*University of Augsburg*), V. Eyert (*University of Augsburg*), N. Blümer (*University of Mainz*), A.K. McMahan (*LLNL*), R.T. Scalettar (*UC Davis*), Th. Pruschke (*University of Augsburg*), V.I. Anisimov (*Yekaterinburg*), and D. Vollhardt (*University of Augsburg*) on **"Realistic investigations of correlated electron systems with LDA + DMFT**. Please see the table of contents for further details.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

http://psi-k.dl.ac.uk/

In these pages one can also find information on how to apply for funding to make collaborative visits.

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

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

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

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

2 News from the Research Training Network 1 (RTN1)

"COMPUTATIONAL MAGNETOELECTRONICS"

2.1 RTN1 Meeting/Workshop/Conference Announcements

2.1.1 Summer School on NEW MAGNETICS

September 15-19, 2003

Bedlewo near Poznan, Poland

Organizers:
Andrzej Jezierski, Andrzej Kowalczyk
Inst. of Molecular Physics, Polish Acad. of Sciences, Poznan, Poland
and
Stefan Bluegel
Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Germany

Sponsored by:
Centre of Excellence MMMFE
ESF Psi-k Programme
RT-Network "Computational Magnetoelectronics"

Invited speakers:

K. Baberschke, *Berlin, Germany*
S. Bluegel, *Juelich, Germany*
P.H. Dederichs, *Juelich, Germany*
H. Ebert, *Muenchen, Germany*
O. Eriksson, *Uppsala, Sweden*
H. Eschrig, *Dresden, Germany*
V. Eyert, *Augsburg, Germany*
J.-M. Greneche, *Le Mans, France*
J. Hafner, *Wien, Austria*
T. Jungwirth, *Prague, Czech Republic*
J. Kirschner, *Halle/Saale, Germany*
H. Kroha, *Bonn, Germany*
H. v. Loehneysen, *Karlsruhe, Germany*
K.-H. Mueller, *Dresden, Germany*
L. Nordstroem, *Uppsala, Sweden*
F. Petroff, *Orsay, France*
A. Slebarski, *Katowice, Poland*
Z. Szotek, *Daresbury, U.K.*
W. Temmerman, *Daresbury, U.K.*
I. Turek, Brno, *Czech Republic*
R. Wiesendanger, *Hamburg, Germany*

The School is thought to be an international forum for presentation and discussion of novel scientific ideas and experimental results of new magnetic materials. The programme of school will cover the following topics: magnetism of correlated electron systems (beyond LDA), multilayers, nanostructures, low-dimensional magnetic systems, magnetic semiconductors, half-metallic systems, f-electron systems, surface magnetism, magnetic anisotropy, non-collinear magnetism, magnetoelectronics, transport in nanostructures, new development in electron spectroscopy and application of new magnetic materials for future electronics.

The main objective of the School is to bring together scientists from the Western, Central and Eastern European countries involved in research and application of novel magnetic materials.

The programme of the School is planned to consist of plenary and contributed talks as well as poster presentations. The proceedings including plenary talks and selected contributed papers will be published at the end of 2003.

Total cost of the School is 350 EUR and 250 EUR (reduced fee for students, postdocs and accompanying persons). The fee covers accommodation in hotel, meals and proceedings.

Timetable

10th April 2003 - abstract submission and registration deadline
5th May 2003 - notification about acceptance of the abstract
10th May 2003 - deadline for payment of fee
15th June 2003 - deadline for paper

For details, see the web site: http://www.ifmpan.poznan.pl/mmmfe/nm.html

or directly:

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3 News from the ESF Programme

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

3.1 Reports on ESF Meetings/Workshops/Conferences

3.1.1 Report on Meeting of Work Group 15

Ab initio design of structural materials

FEBRUARY 14-15, 2003
Ångströmlaboratoriet, Uppsala, Sweden

A start-up meeting of Work Group 15 ”Ab inito design of structural materials” (http://psi-k.dl.ac.uk/proposal/WG15.htm) of a new ESF Programme ”Towards atomistic materials design” (Psi-k) took place in Uppsala, Sweden, February 14- 15, 2003.

The main question of the two-days workshop was ”What is *ab initio* design of structural materials?” During the opening session, particular examples of applications of the first-principles electronic theory for the investigations of technological materials and/or problems within materials sciences relevant for the industry were presented and discussed. In particular, two speakers presented their theoretical works that lead to patent applications. State-of-the-art DFT- based methods for electronic structure and phonon calculations were presented at the first afternoon session, while the second afternoon session was dedicated to methods that go beyond the standard DFT-schemes. During the opening session of the second day we discussed in details possibilities to combine ab initio calculations with phenomenological schemes, because currently this combination seems to be the most efficient way to solving problems for highly complex technological materials. Applications to heterogeneous systems were presented at the second session. At the last session of the meeting we discussed applications of our methods to the design of nuclear materials. Speakers were encouraged to spend some time on the issue regarding the usefulness of the obtained results for the customers of their research. They were also encouraged to communicate basic contents of the works so that the audience can pick up ideas for potential joint work. The workshop provided a possibility for discussions between participants regarding future bilateral collaboration and /or teambuilding.

As a conference organizer, I would like to thank Elisabeth Bill, Sam Shallcross, Erik Holmström, Weine Olovsson, and S. I. Simak for their great help in making things work. The meeting was supported financially by ESF Programme ”Towards atomistic materials design” (Psi-k) and by the Swedish Research Council (VR). I would also like to thank the Physics Department, Uppsala University for housing our meeting.

Igor A. Abrikosov
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E-mail: Igor.Abrikosov@fysik.uu.se

List of Participants

I. A. Abrikosov	Sweden
Artem Baranov	Germany
Thomas Bligaard	Denmark
Michele Catti	Italy
H. Dreyssé	France
H. Ebert	Germany
H. Hugosson	Switzerland
M. I. Katsnelson	Sweden
Adam Kiejna	Poland
Janos J. Kollár	Hungary
Juan J. Novoa	Spain
V. Oison	France
Pär Olsson	Sweden
Nicolas Papanicolaou	Greece
Krzysztof Parlinski	Poland
Alain Pasturel	France
Anthony T. Paxton	United Kingdom
Hariton Polatoglou	Greece
G. Roma	France
A. V. Ruban	Denmark
S. I. Simak	Sweden
V. S. Stepanyuk	Germany
Sangeeta Sharma	Austria
Yu. Kh. Vekilov	Russia
Levente Vitos	Hungary
Perla Wahnón	Spain
F. Willaime	France
Rudolf Zeller	Germany

Polhemsalen. February 14, 2003.

Conference opening

09.00-09.25	Igor Abrikosov (Sweden)	Introductory remarks about WG15, "*Ab initio* design of structural materials."

Ab initio materials design. General applications.

09.25-09.50	G. Roma (France)	Simulation tools for the prediction of the aging of nuclear materials: from *ab initio* calculations to event Monte Carlo simulations.
09.50-10.15	Håkan Hugosson (Switzerland)	Hardness enhancement in transition metal carbides and nitrides by phase stability tuning.
10.15-10.40	Anthony T. Paxton (UK)	Zirconia and Perovskite.
10.40-11.10	**Coffee break. Discussion.**	
11.10-11.35	Perla Wahnón (Spain)	Novel Intermediate Band Materials for High Efficiency Solar Cells Designed by First Principles.
11.35-12.00	Thomas Bligaard (Denmark)	Combined DFT and Evolutionary Search for Materials Design.
12.00-14.00	**Lunch.**	

DFT-based methods for electronic structure and phonon calculations.

14.00-14.25	Rudolf Zeller (Germany)	The Juelich Full-Potential KKR Programs
14.25-14.50	Levente Vitos (Hungary)	EMTO-CPA method: an implementation and selected applications.
14.50-15.15	Krzysztof Parlinski (Poland)	Phonons dispersion curves, soft modes, and phase transitions.
15.15-15.45	**Coffee break. Discussion.**	
15.45-16.10	H. Ebert (Germany)	The Munich SPR-KKR program package: Recent developments and future extensions.

Is there an alternative to DFT?

16.10-16.35	M. I. Katsnelson (Sweden)	Realistic description of strongly correlated materials.
16.35-17.00	Juan J. Novoa (Spain)	Theoretical study of the Magnetism in Molecular Materials using ab initio Quantum Chemical Methods.
17.00-17.25	Michele Catti (Italy)	Piezoelectric and ferroelectric properties of crystals by ab initio periodic LCAO calculations.
17.25-18.00	**Discussion.**	

Polhemsalen. February 15, 2003.

Quasi *ab initio* approach to materials design.

09.00-09.25	Nicolas Papanicolaou (Greece)	Semi-empirical interatomic potentials from first-principles total- energy calculations.
09.25-09.50	V. S. Stepanyuk (Germany)	Magnetism, Structure and Interactions on the atomic scale.
09.50-10.15	A. V. Ruban (Denmark)	Configurational thermodynamics of metallic alloys from first-principles.
10.15-10.40	S. I. Simak (Sweden)	Ordering in multicomponent alloys from first-principles.
10.40-11.10	**Coffee break. Discussion.**	

Ab initio design: Applications to heterogeneous systems.

11.10-11.35	H. Dreyssé (France) and V. Tokar (France)	How to describe self- organisation in heterogeneous systems.
11.35-12.00	Janos Kollár (Hungary)	Materials design in the calculation of surface stress and structural instabillities of perovskites.
12.00-12.25	Adam Kiejna (Poland)	Absorbate structures on metal and oxide surface.
12.30-13.30	Lunch	
13.30-13.55	Sangeeta Sharma (Austria)	Non-linear and linear optical properties of semi-conductor superlattices.
13.55-14.20	Yu. Ku. Vekilov (Russia)	Quasicrystals and their applications.
14.20-14.55	Hariton Polatoglou (Greece)	Investigations of defects in epitaxially grown GaN.
15.00-15.30	Coffee break. Discussion.	
15.30-15.55	Artem Baranov (Germany)	Cobolt nanoislands on Cu(111).

Ab initio design: Applications to nuclear materials.

15.55-16.20	V. Oison and (France) F. Willaime (France)	*Ab-initio* calculations of defects and diffusion in metals: a thourough study of vacancies in Iron.
16.20-16.55	G. Roma (France)	A first principals study of native defects, concentrations, self- doping, and diffusion in alpha-quartz.
16.55-17.20	Pär Olsson (Sweden)	Reactor materials.
17.20-17.30	**Closing remarks.**	

Introductory remarks about WG15, "*Ab initio* design of structural materials?"

I. A. Abrikosov
Condensed Matter Theory Group, Physics Department,
Uppsala University, Box-530, S-75121 Uppsala, Sweden.

Abstract

Working group (WG) 15 "*Ab initio* design of structural materials" is a new group within the new ESF Programme "Towards Atomistic Materials Design (Psi-k)". Originally, 28 scientists from 14 countries expressed their interest in the activities of the WG. I will describe the role of working groups within the network. It is important to realize that the WG is not something pushed onto people. It is there if people want to use it: an opportunity to help stay at the very forefront of research. And at present it exists on paper only – it is up to people to make it a working reality if they want to (quoting Volker Heine). I will discuss what Psi-k expects from the WG, and also what kind of support may be provided for the WG. Some directions for possible collaborations will be indicated, including the development of *ab initio* and *quasi ab initio* methods, an assembly of *ab initio* data bases, and a search for new theoretical approaches towards materials design. I will argue that the most fundamental part of our activities should be aimed at the development of an understanding of correlations between external parameters and materials properties, formulated in a physically transparent way. I will illustrate what I mean by the last statement with examples.

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Simulation tools for the prediction of the aging of nuclear materials: from ab-initio calculations to event Monte Carlo simulations

G. Roma
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Abstract

A large variety of typical materials science problems arise in domains linked to civil nuclear technology; materials properties, like plasticity in metal alloys or resistance to fracture in oxide glasses, are driven by phenomena that have to be studied on several length scales: corrosion, diffusion, phase separation, dislocation dynamics. Moreover, irradiation influences greatly all these phenomena and thus material properties, by altering the population of defects in materials, exciting electrons and phonons, attaining sometimes the complete amorphisation of a crystalline sample. We will present a few case studies where atomistic simulation results —like defect formation and migration energy— are coupled to meso- or macro-scopic models/simulations —like transition state theory, chemical kinetics or events Montecarlo— in order to obtain predictions for real materials of interest.

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Hardness enhancement in transition metal carbides and nitrides by phase stability tuning.

H. Hugosson
Laboratory of Computational Chemistry and Biochemistry,
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Abstract

We here detail a novel mechanism, predicted from first principles calculations, to enhance hardness in transition metal carbide and nitride coatings. Using the technologically important hard transition metal carbides and nitrides as prototypes, though the principle is transferable also to other systems, we have discovered multi-phase/polytypic alloys where several crystal structures have the same or similar total energies. These multi-phase/polytypic, or stacking-fault rich, alloy regions allow the formation of carbide/nitride films with a random or controllable stacking sequence of atomic layers. This can be used to create novel polystructural superlattices without changing the chemical composition, producing systems where the propagation of dislocations will be strongly suppressed by a large number of interfaces between different structures with different glide systems.

The follow-up to this theoretical work is a, perhaps rare, example of theoretical design of materials, where some of the suggested alloys have been produced using modern thin-film techniques, in this case physical or chemical vapor deposition (PVD/CVD). The produced coatings have also, as predicted, been shown to exhibit an enhanced hardness, a materials characteristic that is one of the key properties in these industrially important materials.

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Zirconia and Perovskite

Anthony T. Paxton
Atomistic Simulation Group, Department of Pure and Applied Physics,
Queen's University, Belfast BT7 1NN, U.K.

Abstract

I will talk about recent and not-so-recent tight-binding and LMTO calculations of crystal structures, defect structures, phase transitions and stabilisation of cubic zirconia; surface reconstructions and stoichiometry of (100) surfaces of strontium titanate.

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Novel Intermediate Band Materials for High Efficiency Solar Cells Designed by First Principles

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Abstract

The aim of this work is to study at atomic level, the characteristics of novel photovoltaic semiconductor materials that present an isolated half-filled intermediate band located in the host semiconductor energy band gap. It has been already established [1] that an intermediate band solar cell capable to absorb two energy photons with less energy that the band gap, could improve the optoelectronic properties by producing one additional electron-hole pair compared to the single gap solar cells. Our final purpose is to determine the potential for photovoltaic conversion of this kind of structure by establishing its limiting efficiency.

To reach that, we investigate within DFT quantum mechanical framework, the possibilities of this type of semiconductor material with intermediate band (MIB). In a previous work [2], using an accurate First Principles method to compute band structure and parameters, we proposed an alloy semiconductor containing Ti atoms, of the type: $TiGa_mX_n$ with $X = As$ or P, that presents an isolated half filled intermediate band. A limiting efficiency of 52% has been found in some of these compounds using a procedure of calculation developed in a previous work [3].

Our purpose here, is to present band diagram properties and phonon dispersion studies for others several MIB semiconductor compounds of similar characteristic as before or formed from different semiconductor structure like Si-clathrates. For this work, we use the ab-initio Siesta [4] code based on density functional techniques. In such a method the exchange and correlation energy is calculated in the LDA and GGA approximation. The Siesta code builds up the force constant matrix needed to determine the phonon dispersion diagram.

[1] A. Luque and A. Martí, Phys. Rev. Lett. **76** 5014 (1997).

[2] P. Wahnón and C. Tablero, Phys. Rev. B. **65** 165115 (2002).

[3] C. Tablero, P. Wahnón, L. Cuadra, A. Martí, J. Fernández and A. Luque, Proc. 16th EC Photovoltaic Solar Energy Conf. Munich, James & James, London, p.296-299, 2002.

[4] D. Sanchez-Portal, P. Ordejón, E. Artacho and J.M. Soler, Inst. J. Quantum Chem. **65**, 453 (1997)

Contact person: Perla Wahnón, perla@etsit.upm.es

Combined DFT and Evolutionary Search for Materials Design.

Thomas Bligaard, Gisli Johannesson, Andrei Ruban,
Hans Skriver, Karsten Jacobsen and Jens Nørskov
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Building 307, Technical University of Denmark, 2800 Lyngby.

Abstract

We demonstrate that electronic structure codes have reached a level of high speed and reliability. This allows for the construction of large data bases of "computational" materials and the use of efficient search metods to optimize materials with respect to specific properties directly from first principles. An evolutionary algorithm is developed for use in combination with calculational tools of electronic structure theory. The evolutionary algorithm is used to search for ordered alloys with specific properties. Based on an unbiased initial population of materials, the algorithm creates new populations of materials and quickly locates a part of the phase space of material composition yielding interesting material properties. Pareto-optimality is then introduced as a natural method for selecting materials, when the optimization is performed with respect to several properties simultaneously . The Pareto-analysis is used on a data base of 64,000 calculated ordered alloys to yield the materials which should be the most interesting for a specific industrial process.

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The Jülich Full-Potential KKR Programs

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IFF, 52425 Jülich, Germany.

Abstract

An overview will be given over the present state and the applicabilities of the Jülich KKR Green-function programs. It will be shown that forces and lattice relaxation in crystals perturbed by impurities can be calculated in very good agreement with plane-wave pseudo-potential calculation. It is also shown that lattice constants and bulk moduli of metals and semiconductors can be calculated in very good agreement with the FLAPW method. It is further demonstrated that the tight-binding (TB) version of the KKR method (similarly to the TB-LMTO method) allows for density-functional calculations for slabs, surfaces, interfaces, and semi-infinite crystals with a computational effort which linearly scales with system size.

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EMTO-CPA method: an implementation and selected applications.

Levente Vitos
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Abstract

Within the frameworks of the Exact Muffin-Tin Orbitals (EMTO) Theory and the Coherent Potential Approximation (CPA) we have developed a total energy method for random alloys. The accuracy of the EMTO-CPA method is demonstrated through test calculations performed on Cu-Zn and Ag-Zn binary alloys. The present theoretical results for the elastic properties of random alloys are in very good agreement with the available experimental data.

We use the EMTO-CPA ab-initio method to establish a theoretical insight to the electronic structure of austenitic stainless steels. We map the elastic properties of Fe-Cr-Ni alloys as functions of chemical composition. The so generated data can be employed in the search for new steel grades, and as example, we predict new compositions with outstanding properties among the austenitic family of stainless steels.

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Phonon dispersion curves, soft modes and phase transitions.

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Abstract

The DFT method was used to predict the lattice dynamics of the crystal, together with the direct method and the Hellmann-Feynman forces created by diplaced atoms. The phonon dispersion curves of GaN were predicted before confirming them by X-ray inelastic scattering measurements. We found that in SnO_2 a soft mode accompanies the ferroelastic phase transition occuring under pressure. Phonon dispersion curves and phonon density of states can be calculated in as complex crystals as tetragonal chalcopyrites ($CuInSe_2$, $AgGaS_2$, $AgGaSe_2$), orthorhombic minerals $MgSiO_3$, cubic minerals Mg_2SiO_4, and ferroelectric material $LiNbO_3$. These results give patterns for the Raman and infrared absorbsion spectra describing the frequencies and irreducible representations of the zone-center modes. They also allow to calculate the thermodynamical functions and the Debye-Waller factors, and predict to some extend the properties under finite temperature. Calculations of partial phonon density of Fe ions in antiferromagnetics $FeBO_3$ allowed to prove that indirectly the magnetic inteaction may quit essentially influence the phonon frequency spectrum measured by inelastic nuclear absorption. For the first time we have calculated the phonon dispersion curves of the well-known shape memory intermetalic alloy $NiTi$. Austenite, martensite and

R-phase of $NiTi$ were analized, and the phase transition temperature between martensite and R-phase has been found. These examples illustrate the application of DFT and direct method (phonon calculations) in finding and predicting material properties. See also PHONON program: http://wolf.ifj.edu.pl/phonon/.

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The Munich SPR-KKR program package: recent developments and future extensions.

H. Ebert, D. Binea, S. Chadov, M. Kosuth, S. Mankovskyy,
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Abstract

A short overview on the underlying formalism of the Munich spin-polarised relativistic (SPR) KKR-program package is given. A description of the various features will be illustrated by corresponding results on various kinds of transition metal systems with an emphasise on spin-orbit induced and magnetic properties. As new features of the program package the treatment of spin spirals, the full potential mode and implementation of the rotational invariant $LDA+U$-scheme will be presented. An outlook on future extensions - in particular the combination with the Jülich TB-KKR program - will be given as well.

Finally, a short description of the accompanying graphical user interface xband, that is programmable and easily adaptable to other program packages, will be given.

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Realistic description of strongly correlated materials.

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Abstract

The Local Density Approximation (LDA) for the electronic structure calculations has been highly successful for non-correlated systems. The LDA scheme quite often failed for strongly correlated materials containing transition metals and rare-earth elements with complicated charge, spin and orbital ordering. We discuss recent progress beyond the static density functional approximation, which includes finite temperature effects related to the charge, spin and orbital fluctuations in a self-consistent manner. Dynamical mean field theory (DMFT) in combination with the first-principle LDA scheme (LDA+DMFT) can be a starting point for the construction of a new spectral density functional for a realistic description of various correlated electron materials.

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Contact person: Alex Lichtenstein, A.Lichtenstein@sci.kun.nl

Theoretical study of the Magnetism in Molecular Materials using *ab initio* Quantum Chemical Methods.

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Abstract

The current knowledge about the mechanism of magnetism in purely organic materials, as provided by quantum chemical ab initio calculations, is presented. The microscopic basis of magnetism in this compounds will be presented. The study of the magnetic interactions on various prototypical crystals are provided to illustrate the potential and failures currently methodology.

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Piezoelectric and ferroelectric properties of crystals by ab initio periodic LCAO calculations.

Michele Catti
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Abstract

First-principles simulations of crystal piezoelectricity are a comparatively novel achievement of the computational solid state science, which has been made possible by important theoretical advances in the understanding of electrical polarization in crystals from the quantum- mechanical point of view [1,2]. The outstanding importance of piezoelectric properties in several branches of materials science and technology is well known; however,

although in principle any non-centrosymmetrical crystal may show piezoelectric behaviour, the number of available experimental data is limited. For this reason, a new impulse to research in this field is expected from ab initio theoretical methods able to predict piezoelectric constants.

Piezoelectricity is the change of electric polarization state of a crystal as a response to applied stress or strain. The piezoelectric properties are usually represented by two types of third-rank tensor components: $d_{ik} = P_i \tau_k$ and $e_{ik} = P_i \epsilon_k$, where P_i is the i^{th} Cartesian component (i=1,..3) of the electric dipole moment per unit volume $\mathbf{P}$, τ_k and ϵ_k (k=1,...6) are stress and strain tensor components (Voigt contraction of indices is understood), respectively. The two sets of d_{ik} (stress-related) and e_{ik} (strain-related) piezoelectric constants are transformed into each other according to $d_{ik} = \sum_{h(1,6)} e_{ih} s_{hk}$, where the s_{hk} coefficients (h,k=1,..6) are the elastic compliances or components of the inverse matrix of the elastic constants ($s = c^{-1}$). Theoretical calculations of piezoelectric constants usually concern the eik coefficients, because constant strain conditions are easier to simulate than those at constant stress. Only changes of polarization intensity $\triangle\mathbf{P}$ have physical meaning; as reference state, the undeformed crystal structure is chosen.

The modern theory of spontaneous polarization (ferroelectricity) and of piezoelectricity in dielectrics is based on either the Berry phase or the Wannier functions approach. Both methods have been implemented in the new version of the CRYSTAL code [3], which is based on the solution of periodic self-consistent-field one-electron equations employing both Hartree-Fock and Density-Functional-Theory Hamiltonians coupled with an all-electron basis set of localized Gaussian functions (Linear Combination of Atomic Orbitals). Calculations have been performed on ZnO and ZnS, both in the wurtzite $P6_3mc$ and in the zinc blende $F\overline{4}3m$ structures. In the first case, the e_{33}, e_{31} and e_{15} constants are obtained, and in the second one the e_{14} value. Suitable lattice deformations had to be chosen, in order to minimize the symmetry loss of the crystal structure. A good agreement with experimental data was obtained, and the quality of results is analyzed in detail.

[1] R. Resta, Rev. Mod. Physics **66**, 899 (1994)

[2] D. Vanderbilt, J. Phys. Chem. Solids **61**, 147 (2000) [3] V.R. Saunders et al., CRYSTAL98: User's manual. University of Torino, Italy, and CLRC Daresbury Laboratory, UK. (1999)

Contact person: Michele Catti, catti@mater.unimib.it

Semi-empirical interatomic potentials from first-principles total-energy calculations.

N. I. Papanicolaou
Department of Physics, University of Ioannina,
P.O. Box 1186, GR-45110 Ioannina, Greece.

Abstract

We present semi-empirical interatomic potentials for simple, transition and noble metals, along with for ordered binary alloys in the framework of the second-moment approximation of the tight-binding theory. The potentials were obtained by fitting to the total energy of these materials computed by first-principles augmented-plane-wave calculations as a function of

the volume. The scheme was validate by calculating the bulk modulus, the elastic constants and surface energies of the pure metals and alloys that were found to be in agreement with the experiment. We also have performed molecular-dynamics simulations at various temperatures, deducing the thermal expansion coefficient, the temperature dependence of the atomic mean-square displacements, as well as the phonon density of states and the phonon dispersion curves of the compounds. In addition, we have studied the self-diffusion of single adatoms on low-index surfaces and we have determined the migration energies and pre-factors for various diffusion mechanisms. Despite the simplicity of the model, a satisfactory accuracy was obtained.

Contact person: N. I. Papanicolaou, nikpap@cc.uoi.gr

Magnetism and Structure on the atomic scale

V. S. Stepanyuk
Max-Planck-Institut für Mikrostrukturphysik,
Halle, Germany.

Abstract

If atomic structures have at least one dimension small enough that quantum-mechanical effects prevail, their behaviour can be particularly interesting. In this talk we demonstrate several magnetic and structural effects on the atomic scale. We apply KKR Green's function method to study magnetism and structure of supported clusters and atomic bridges. Interatomic potentials for low-dimensional systems are constructed using ab initio data for selected cluster properties and the tight-binding approximation. Quantum interference and long-range interactions between magnetic adatoms on metal surfaces are investigated. Magnetic properties of atomic bridges are discussed. Scenario of strain relief in mesoscopic magnetic islands is presented.

Contact person: V. S. Stepanyuk, stepanyu@mpi-halle.de

Configurational thermodynamics of metallic alloys from first principles.

A. V. Ruban, H. L. Skriver
Center for Atomic-scale Materials Physics and Physics Department,
Technical University of Denmark, DK-2800 Lyngby, Denmark.
S. I. Simak, S. Shallcross
Condensed Matter Theory Group, Physics Department,
Uppsala University, Box-530, S-75121 Uppsala, Sweden.

Abstract

We discuss the problem of obtaining Ising-type effective cluster interactions from first-principles calculations and present the formalism for the generalized perturbation method (GPM) in the framework of the Korringa-Kohn-Rostoker method in the atomic-sphere and coherent potential approximations (KKR-ASA-CPA) with electrostatic correction due to screened Coulomb interactions. The results for the ordering energies, short-range order parameters and transition temperatures of the Cu-Zn, Cu-Au and Pt-Co systems obtained by this method, indicate that it is an efficient and accurate *ab initio* technique for studying ordering effects in metallic alloys where the local environment effects are small and the CPA is adequate.

Contact person: Andrei Ruban, ruban@fysik.dtu.dk

How to describe self-organisation in heterogeneous systems.

Hugues Dreyssé and Vasyl. I. Tokar
Institut de Physique et Chimie des Materiaux de Strasbourg,
23 rue du Loess, 67034 Strasbourg, France.

Abstract

Since the number of atoms in nanostructures or glassy media is large, the description in the real space requieres the use of many continuous atomic coordinates. The later task is known to be computationaly very demanding. In order to be able to use the efficiency of the Monte Carlo simulations for strained epitaxial growth, we show that in the case of coherent deposition the system can be mapped on a lattice-gas model with a discrete energy spectrum leading to the appearance of cluster interactions. A recursive approach leads to a very fast determination of the relaxation energy of very large systems. For strong lattice size mismatch the largest term is a triplet repulsive linear term. An attractive chemical pair interactions induces frustrations and leads to kinetic glassy phenomena, such as gelation and ageing. The size of the precusor platelets of quantum dots is also obtained and discussed.

The determination of these multiatomic interactions from the electronic structure will be adressed.

Contact person: Hugues Dreyssé, Hugues.Dreysse@ipcms.u-strasbg.fr

Materials design in the calculation of surface stress and structural instabilities of perovskites.

J. Kollár
Research Institute for Solid State Physics and Optics,
H-1525 Budapest, P.O.Box 49, Hungary.

Abstract

The aim of materials design is to determine the microscopic input conditions (structure, concentrations, etc.) for creating a material with required macroscopic properties. We have carried out these kind of studies in two different areas:

- Surface stress calculations (in cooperation with R. Ahuja and L. Vitos)
- Structural instabilities of perovskites (in cooperation with Blanka Magyari-Köpe and L. Vitos)

In surface stress calculations one possible application of materials design is to create surfaces with a required surface stress (e.g. zero). To achieve this aim we have worked out a method to calculate surface stress using *exact muffin-tin orbitals* (EMTO) *full charge density* (FCD) slab calculations and applied it for fcc transition metal surfaces.

In the field of structural instabilities of perovskites our aim was to explain the discontinuities within the lower mantle of the Earth at certain pressure and temperature values. The main ingradients of the lower mantle are perovskites with orthorhombic structure ($MgSiO_3, CaSiO_3$ with Fe, Al, etc.). As a result of our EMTO-FCD calculations we give a possible explanation for the structural changes of provskites within lower mantle conditions.

Contact person: J. Kollár, jk@ppc1.szfki.kfki.hu

Structural materials via adsorption and growth at surfaces.

Adam Kiejna
Institute of Experimental Physics, University of Wrocław,
Poland.

Abstract

The adsorbate-adsorbate and adsorbate-substrate interactions and bonding at metallic surfaces and the metal/oxide interface are of crucial importance in advanced applications in materials science, nanotechnology and materials science. These include the possibility of better tuning catalytic properties of materials, a closer understanding of structure formation, oxidation and corrosion. In this talk some examples will be presented of the exploration of early stages of oxidation of Al(111) and Mg(0001) surfaces, and stability of the ultrathin aluminum oxide films on Al(111). For Mg(0001) surface oxidation we show that oxygen is immediately incorporated into the Mg surface, even at very low coverages, and we also find a hitherto unknown surface phase of Mg oxide consisting of mixed oxygen-magnesium layers on top of an almost unchanged Mg(0001) surface. The formation and coupling mechanism between the adsorbate chains at the Mo(112) surface will be briefly discussed. Finally, results regarding the fractal-like growth of Cu islands on W(110) surface obtained by kinetic Monte Carlo simulations will be presented.

Contact person: Adam Kiejna, kiejna@ifd.uni.wroc.pl

Linear and Second-order Optical Response of the III-V Mono-layer Superlattices.

S. Sharma
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Universitätsplatz
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Abstract

We report the first fully self-consistent calculations of the nonlinear optical properties of superlattices. The materials investigated are mono-layer superlattices with GaP grown on the the top of InP, AlP and GaAs (110) substrates. We use the full-potential linearized augmented plane wave method within the generalized gradient approximation to obtain the frequency dependent dielectric tensor and the second-harmonic-generation (SHG) susceptibility. The effect of lattice relaxations on the linear optical properties is studied. Our calculations show that the major anisotropy in the optical properties is the result of strain in GaP. This anisotropy is maximum for the superlattice with maximum lattice mismatch between the constituent materials. In order to differentiate the superlattice features from the bulk-like transitions an improvement over the existing effective medium model is proposed. The superlattice features are found to be more pronounced for the second-order than the linear optical response indicating the need for full supercell calculations in determining the correct second-order response. We have also rearranged the existing equations for calculation of the SHG susceptibility so as to reduce the computational requirements substantially. some results of the bench marking are also presented.

Other than that I would also discuss the existing computational tools that our group has for calculating various properties of the designer materials.

Contact person: Sangeeta Sharma, sangeeta.sharma@uni-graz.at

Quasicrystals and their applications.

Yu. Kh. Vekilov
Dept. Theoretical Physics, Moscow Steel and Allot Inst.,
11, Leninski Prospect, Moscow 119996, Russia.

Abstract

The potential applications of quasicristals are considered. Quasicrystals possess physical properties such as low electrical and thermal conductivities, low coefficient of friction, selective reflectance of light, high hardness, etc. This defines their potential applications as new fillers for high wear plastics and steels, selective absorberes of light, coating materials, thermal barriers, hydrojen storage materials, etc.

Contact person: Yuri Vekilov, yuri_vekolovyahoo.com

Investigation of defects in epitaxially grown GaN.

Hariton Polatoglou
Phys. Dept., Aristotle University of Thessalonki,
Gr-54124, Greece.

Abstract

The Stillinger-Weber empirical potential was modified and its parameters were determined to achieve a realistic description of the microscopic structure and the energetics of different planar defects and their interactions in wurtzite GaN. The formulation was based on the adjustment of the parameters in order to represent the Ga-Ga, N-N and Ga-N bonds. The input data comprises of the different crystalline phases of gallium, nitrogen and GaN. A satisfactory agreement on the values of the energy versus atomic volume per atom was obtained compared to those derived by ab-initio calculations and experimental data for all the cases studied. By employing the modified Stillinger-Weber potential the energy of translation domain boundaries, which have been observed experimentally in GaN thin films, was calculated providing results comparable with ab-initio calculations. The energies of inversion domain boundaries and of the I1 stacking fault on the basal plane were calculated and compared to those of ab initio calculations from the literature. The potential was then applied for relaxation of large supercells comprising junction lines between inversion domain boundaries and stacking faults. The relaxed structures were used for HRTEM image simulations, which were compared with the corresponding experimental observations.

Contact person: Hariton Polatoglou, hariton@auth.gr

Cobalt nanoislands on Cu(111)

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Fachbereich Physik,
Martin-Luther-Universität,
Friedemann-Bach-Platz 6, D-06099 Halle, Germany.

Abstract

The knowledge of the structure and electronic states of Co islands on Cu surfaces is of great importance for the understanding of the transport of electrons across the Co/Co interface.

Performing atomic scale calculations, we demonstrate that mesoscopic relaxations in Co islands on Cu(111) significantly affect the shape of clusters and the substrate.

Electronic states of Co islands are investigated by means of the KKR Green's function method. We reveal that electronic surface states are spin-polarized. A very strong intensity of the surface state found in our work may be of great importance in tunneling magnetoresistance devices. A quantum interference of surface states electrons near Co islands is discussed. Our results are in a good agreement with the recent STS experiments.

Contact person: A. N. Baranov, baranov@hera.physik.uni-halle.de

Ab initio calculations of defect and diffusion in metals : a thorough study of vacancies in iron.

Vincent Oison and François Willaime
Service de Recherches de Métallurgie Physique, CEA/Saclay,
91191 Gif-sur-Yvette, France.

Abstract

We have performed a detailed ab initio study of the structure and energetics of vacancies in α-iron both in the LDA and GGA approximations using the PWSCF planewave pseudopotential code. For the vacancy formation energy a rather large discrepancy is found between the LDA and GGA values (2.4 eV and 1.9 eV), as compared to other transition metals. Both values are in good agreement with experimental data obtained in the ferromagnetic state on carbon-free samples (2.0 ± 0.2 eV). The migration path is shown to be single-bumped but rather flat for both functionals, and the values obtained for the migration energy (0.7 eV and 0.6 eV) are in excellent agreement with experiments. The vibrational modes around the vacancy have been computed using the DFPT formalism. A low frequency vibration mode, localized on the nearest-neighbour of the vacancy, with tetrahedral symmetry has been evidenced. The resulting self-diffusion coefficients are critically discussed in comparison with experiments.

This study is part of a project aiming at using ab initio calculations to determine the structure and energetics of primary defects (vacancies and interstitials) produced under irradiation. These data can be used to parametrize Kinetic Monte Carlo models for the simulation of the aging of these materials (pressure vessel steels in the present case)

Contact person: Vincent Oison, vincent.oison@cea.fr

A first principles study of native defects, concentrations, self-doping, and diffusion in alpha-quartz

G. Roma
Service de Recherches de Métallurgie Physique, CEA/Saclay,
91191 Gif-sur-Yvette, France.

Abstract

We present first principles calculations of formation energy of silicon and oxygen vacancies and interstitials in α-quartz, in several charge states. We show a few unknown structures of some defects, namely silicon defects, and discuss specific features like the effect of charge on the formation volumes as resulting from our calculations. We take into account the influence of defect concentrations on the Fermi energy by solving numerically the equation imposing charge neutrality and we show the dependence of the Fermi energy and the resulting defect concentrations on temperature and oxygen partial pressure. We present migration energies for defects who are supposed to be most important for diffusion and we discuss the possible implications on ionic conductivity in SiO_2.

Contact person: Guido Roma, guido.roma@cea.fr

Reactor materials.

Pär Olsson
Department of Neutron Research, Ångström Laboratory,
Uppsala University, Box 525, SE-75120 Uppsala, Sweden.

Abstract

In the business of reactor materials it is the future reactors that provide the challenge and the motivation. Future fusion and transmutation reactors will present a new kind of working environment for materials: high and hard neutron fluxes. The materials of today are not sufficiently resistant to neutrons to be economically viable.

The most promising materials of today are based on Fe-Cr alloys of up to 12 at.% Cr. We are studying the properties of Fe-Cr alloys by doing *ab initio* calculations with the EMTO-CPA method, among others. Our first results show that there is a range of negative mixing enthalpy from pure Fe up to about 8% Cr. In the same region we have a minimum in the bulk modulus which is consistent with experiments. The data from our calculations has been used to fit a new EAM potential for Fe-Cr.

Contact person: Pär Olsson, olsson@tsl.uu.se

3.2 ESF Workshop/Conference Announcements

3.2.1 Hands-on Berlin Workshop

Final Announcement

APPLICATION OF DENSITY-FUNCTIONAL THEORY IN CONDENSED MATTER PHYSICS, SURFACE PHYSICS, CHEMISTRY, ENGINEERING AND BIOLOGY

21 - 30 July 2003, Berlin

This hands-on workshop comprises

1) lectures on DFT basics AND on methodology; special emphasis will be given to a comparison of different codes (for example, LAPW, PAW, DMol3, pseudopotentials)

2) hands-on practical sessions, so that the participants get familiar with all aspects of running DFT total energy calculations.

For more information see the announcement

http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/announcement.html

and/or the preliminary program

http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/workshop-program.html

Dr. Catherine Stampfl
Fritz-Haber-Institut
der Max-Planck-Gesellschaft
Faradayweg 4-6
D-14 195 Berlin-Dahlem/Germany

phone : ++49-30-8413 4801
e-mail: stampflc@fhi-berlin.mpg.de

3.2.2 Sardinia Workshop

The Physics Department, Università di Cagliari, and the Cagliari Research Unit of Instituto Nazionale per la Fisica della Materia organize the

XIII Workshop on Computational Materials Science

13 - 18 September 2003 [3mm]

Calaserena Village, Geremeas (CA), Sardinia, Italy

web page: http://www.dsf.unica.it/CMS2003

e-mail: workshop@dsf.unica.it

with the sponsorship of

European Science Foundation Programme "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

and

Democritos Modeling Center for Research in Atomistic Simulation

under the patronage of UNESCO

An international workshop on computational techniques and applications to materials science

See TENTATIVE INVITED SPEAKERS and INFO below.

FORMAT: About 20 invited lectures plus TALKS (about 12) and POSTER contributed session.

VENUE: Calaserena Village at Geremeas (CA), an attractive sea resort on the south-eastern coast of Sardinia, providing comforts and an informal atmosphere.

CONTACT: For scientific and logistic queries: workshop@dsf.unica.it

CONTRIBUTIONS: Contributions in poster format are invited. Deadline for abstract submission: July 15, 2003. Contact F. Bernardini at +39 070 6754847, V. Fiorentini at +39 070 6754912 or P. Ruggerone at +39 070 6754869 or at workshop@dsf.unica.it for further details. LaTeX template for abstract can be downloaded from the Workshop homepage:

http://www.dsf.unica.it/CMS2003

INVITED SPEAKERS:

F.J. Himpsel (Madison, USA)
D. Marenduzzo (Oxford, UK)
M. Mareschal (Bruxelles, Belgium)
E. Molinari (Modena, Italy)
C. Molteni (Cambridge, UK)
M. Parrinello (Manno/Zuerich, Switzerland)
A. Pasquarello (Lausanne, Switzerland) (*)
L. Reining (Paris, France)
E. Tadmor (Haifa, Israel)
J.P. Toennies (Goettingen, Germany)
E. Tosatti (Triest, Italy) (*)
D. Wolf (Duisburg, Germany)

(*) not yet confirmed

REGISTRATION and **SUPPORT**:

The REGISTRATION form can be sent directly from the Workshop homepage

(http://www.dsf.unica.it/CMS2003).

The deadline is June 15, 2003.

The registration should be accompanied by payment receipt of the CONFERENCE FEE (by FAX: ++39-070-510171). The fee includes shuttle services (13/9 Cagliari Airport-Hotel, 18/9 Hotel-Cagliari Airport), full-board lodging at Calaserena Village from 13 September to 18 September, coffee breaks, refreshments, and amounts to

Single room	Euro 667,50/person
Double room	Euro 550,00/person
Triple room	Euro 525,00/person
Quadruple room	Euro 525,00/person
Extra meal (if necessary)	Euro 23,25/person

Example: Single room + 1 extra meal = 690.75 (Total fee) .

A very limited number of single rooms is available, we will process the Hotel Reservations on the first-come first-serve basis.

PAYMENT should be effected by bank money transfer, preferably by SWIFT, in EURO net of any bank charges, on the bank account No 22698 of Comitato Organizzatore di Attività di Fisica Computazionale, at Banco di Sardegna (Swift code: SARDIT3S100), Sede di Cagliari, Codice ABI 1015/7 - CAB 04800/9.

No fee is requested from the invited speakers.

The Organizing Committee is able to offer support (from 50% up to 100% of the conference fees plus travel costs in some cases) to a very limited number of young scientists, preferrably PhD students. The deadline for the request of financial support is May 15, 2003. The committee will comunicate its decision on June 1, 2003.

IMPORTANT

If you are not asking for SUPPORT, please fill the Registration Form and the Accomodation Form before the deadline. If you are asking for support, fill the Financial Support Form as soon as possible and wait for approval. If your Support request is approved you have to fill the Accomodation Form (only). Those who have been denied Support have to fill BOTH Registration Form and Accomodation Form if they want to confirm their participation.

Series Chairman : prof. A. Baldereschi - EPFL Lausanne

Workshop Chairman : prof. F. Meloni - INFM and Università di Cagliari

Scientific Secretariat:

dr. F. Bernardini
dr. V. Fiorentini
dr. P. Ruggerone
INFM and Università di Cagliari

First Announcement

3.2.3 Conference on 'AB-INITIO MANY-BODY THEORY FOR CORRELATED ELECTRON SYSTEMS'

25 - 29 August 2003

Miramare, Trieste, Italy

We would like to announce and encourage participation in the Conference on 'Ab-initio many body theory for correlated electron systems' to be held at the Abdus Salam International Centre for Theoretical Physics (ICTP) in Trieste, Italy from 25 to 29 August 2003. This conference is supported by the ICTP and Psi-k. Its overall aim is to communicate the latest technical developments in ab-initio many body calculations and to illustrate this on a few selected applications. The technical topics which will be stressed at this conference are:

Dynamical mean field theory (DMFT) and electronic structure calculations, with applications to d- and f-electron materials;
Recent developments on the GW approximation. This includes in particular issues related to self-consistency, and recent efforts to combine GW with DMFT towards a first-principles electronic structure method for strongly correlated electron systems;
Latest developments and applications of Quantum Monte Carlo methods;
Developments in Density Functional Theory and its implementation: time dependent DFT, "downfolding" on a few-orbital hamiltonian, etc...

Applications of these methods to materials-specific calculations will include:

- transition metals and their oxides;
- f-electron materials;
- fullerenes.

In addition, topical sessions on experimentally active field will be organized on:

- Spectroscopies;
- high pressure studies;
- ferromagnetic superconductors;
- magnetic semiconductors and nanoelectronics, including transport.

CONFIRMED SPEAKERS include:

O.K. Andersen, V. Anisimov, F. Aryasetiawan, T. Dietl, S. Erwin, R. Godby, H. Gross, K. Held, T. Kotani, C. Lambert, T. Le Bihan, I. Mertig, R. Needs, M. Rozenberg, A. Rubio, S. Savrasov, A. Schindlemayer, T. Schultess, K. Syassen, A. Svane, A. Lichtenstein, W. Pickett, D. van der

Marel, G. Zarand, S. Zhang.

ADDITIONAL INFORMATION, REGISTRATION INFORMATION AND A PRELIMINARY PROGRAM can be found on the web at:

`http://www.ictp.trieste.it/~smr1512/`

Antoine Georges and Walter Temmerman

4 News from UK's CCP9 Programme

UK's Collaborative Computational Project 9 on "Computational Studies of the Electronic Structure of Solids"

4.1 Conference Announcements

4.1.1 B.L. Györffy's Event in Bristol

Final Announcement

"Order and disorder in solids: alloys, magnetism and superconductivity"

A celebration of the contributions of Balazs Györffy to theories of the electronic structure of solids

Friday 11 April to Saturday 12 April 2003

This is a final announcement of the Györffy Event. As you may know Balazs Györffy reaches the age of 65 this year. We are arranging a conference at the University of Bristol to celebrate Balazs' contribution to theories of the electronic structure of solids. The title is 'Order and Disorder in Solids: Alloys, Magnetism and Superconductivity' and it will be held Friday 11 April to Saturday 12 April, 2003.

Some details including a photograph (if you have forgotten what Balazs looks like) can be found on the web page

http://www.phy.bris.ac.uk/research/theory/balazs-conference.htm

We are contacting past and present students, postdocs, collaborators, friends and colleagues of Balazs alerting them to this meeting and encouraging them to attend. It should be a very pleasant occasion as well as an excellent scientific gathering and a splendid opportunity to renew your acquaintance with BLG.

We realize that not everyone will be able to attend the whole conference. It is possible to join the Conference Banquet at 19:00 on Friday 11 April 2003. The cost will be 30 pounds. There is a registration form on the WEB pages. If you wish to attend the conference and/or the Banquet please complete the form and return it to Tracie Anderson as soon as possible.

We look forward to welcoming you to Bristol in April.

Professor R Evans (For the Organising Committee)

5 General Workshop/Conference Announcements

5.1 PHYSICS SPRING SCHOOL IN TOULOUSE (PSSIT 2003)

Modeling and Simulation in Micro and Nano Technologies and Materials Engineering

April 7th - 11th, 2003, Toulouse, France

http://www.lpst.ups-tlse.fr/PSSIT

Organized by

LPST/IRSAMC-LAAS-ATOMCAD

Georges Landa
Laboratoire de Physique des Solides de Toulouse (LPST)
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Institut: http://www.irsamc.ups-tlse.fr
SFP: http://www.lpst.ups-tlse.fr/SFP

5.2 Hands-on-FPLO Workshop

March 28 - April 1, 2003

IFW Dresden, Germany

http://www.ifw-dresden.de/FPLO/

We will release FPLO-3, including LSDA+U and CPA options together with the scalar relativistic, highly accurate and efficient minimum basis code. The 4-component variant, RFPLO, will be released as beta- version. Details can be found at the above url and in the highlight section of the Psi-k Newsletter No 52 (August, 2002).

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Email: m.richter@ifw-dresden.de
`http://www.ifw-dresden.de/~manuel`

5.3 Symposium on "Spin-Dependent Electronic Materials"

45th Electronic Materials Conference (EMC)

June 25 - 27, 2003, Salt Lake City, Utah

The 45th Electronic Materials Conference (EMC) aims to provide the premier annual forum for presentations of current interest and significance to the preparation and characterization of electronic materials. The "Spin-Dependent Electronic Materials" symposium aims to bring together scientists, both experimentalists and theoreticians, working in the field of spintronics materials, including diluted magnetic semiconductors, metallic systems, magnetic multilayers.

For more information, please visit the conference web-site at:

http://www.tms.org/Meetings/Specialty/EMC03/EMC03.html.

5.4 One-day Meeting on "New Challenges in Computational Chemistry"

Imperial College London, 11th April 2003

Organized by

The Faraday Division - Royal Society of Chemistry - and the Industrial Physical Chemistry Group

The conference will cover advances in applications of computational Chemistry in Nanotechnology, Polymers, Materials, Pharmaceutical Modelling, Cheminformatics and Biochemistry. The proceedings of the meeting will be published in the Journal Molecular Simulation.

Confirmed speakers at the meeting include:

o Prof U Landman (Georgia Institute of Technology)
"Small is different: Chemistry and Physics at the nanoscale non scalable regime"

o Prof K Kremer (Max Planck)
"Multiscale Modelling in Polymer Science: Status and Perspective"

o Prof N Harrison (Imperial College and Daresbury Lab)
"Recent Progress in electronic structure calculations: density functional theory and beyond"

o Prof D Livingstone (ChemQuest)
"Building Structure activity models with Artificial Intelligence techniques"

o Dr M Hann (GlaxoSmithKline)
"Computational Chemistry and Informatics - tools for drug design and discovery"

o Prof W G Richards (University of Oxford)
"Pattern Recognition and grid computing in drug discovery"

The meeting also includes a poster session. There are still a number of student bursaries available to support attendance at the meeting.

Registration Dates:

Early Registration: by 14 February 2003
Late Registration: by 28 March 2003

Further details and registration forms can be obtained from:

http://www.rsc.org/pdf/faraday/fara008Apr03.pdf

and

Dr Fernando Bresme
Department of Chemistry
Imperial College, SW7 2AY, London, UK
E-mail:f.bresme@imperial.ac.uk

6 General Job Announcements

Two Post-Doctoral and/or PhD-positions available (RWTH Aachen/Germany)

Candidates for the positions are expected to work on one or more of the following topics: i) theoretical modeling of amorphous silicon nitride-based materials; ii) first-principles simulation of phase diagrams of nitrides and oxinitrides and phase transitions at high pressures; iii) first-principles calculations of catalytic reactions in porous silicon imidonitrides.

The projects are funded by the DFG and are (in part) collaborations with experimental groups from chemistry, physics, and engineering.

Applicants should hold a B.Sc. (equiv.) in Chemistry, Physics or a related subject. Primary tool for investigations are density functional methods, especially the plane-wave pseudopotential approach. Successful applicants, therefore, should have demonstrated their interest for theoretical and computational science; for post-docs experience with DFT methods is mandatory. The RWTH Aachen is well equipped with computational infrastructure.

One position is available immediately, the other may start July 2003. Initially, the appiontment will be made for one year, with a possible extension depending on funding. Salary will be orientated on the BAT scale (BAT II/a). Requests for further information and applications should be sent to

Peter Kroll
RWTH Aachen
Anorganische Chemie
Prof.-Pirlet-Str.1
D-52056 Aachen
Germany
E-mail: peter.kroll@ac.rwth-aachen.de
(electronic submission is preferred)

POSTDOCTORAL/PHD POSITION
IN THEORETICAL PHYSICS AT REGENSBURG UNIVERSITY

A postdoctoral or PhD position is available in the theory research group on Complex Quantum Systems within the priority program "Ferromagnet-semiconductor nanostructures" at Regensburg University. The topic of the research project comprises spin-dependent transport in nanostructures and at interfaces. The successful candidate should preferably have a background in Mesoscopic Physics, Spin Electronics, Computational Nanoscience, or a related research direction. The appointment may start in April 2003, or later. The duration for the postdoctoral position is up to 2 years.

Candidates are asked to send an application letter including a CV (postdoctoral candidates additionally: a list of publications and a brief summary of research interests) to the address below. Applicants are also asked to arrange for at least two letters of recommendation to be sent to:

Prof. Dr. Klaus Richter,
Institut für Theoretische Physik,
Universität Regensburg,
93040 Regensburg, Germany,

or by email to:

klaus.richter@physik.uni-regensburg.de.

For further information please contact klaus.richter@physik.uni-regensburg.de.

More information on our present research activities can be found at websites:
http://www.physik.uni-regensburg.de/forschung/richter/richter. Our research at Regensburg University is embedded in a strong research environment in both, theoretical and experimental nanosciences. For further information see: http://www.physik.uni-regensburg.de .

PhD Position - University of Paderborn, Germany

Funding is available for immediate start of a 3 year PhD student position at the university of Paderborn. The research is within the RENiBEl training network in the area of simulation of rare earth dopants in nitride semiconductors.

Recent investigation of light emission from rare earth (RE) doped GaN layers demonstrates the exciting possibility of employing such materials in electroluminescent devices ranging from the near ultraviolet (250 nm) to the near infrared (around 1.5 microns), with one material. Gaining the necessary understanding and control of the properties of the novel RE-doped nitrides presents an important scientific challenge.

The student employed at Paderborn will carry out modeling calculations to support the experimental teams involved. The simulations will make use of modern DFT and DFTB theoretical methods.

The successful candidate will join an EU funded network of experienced European academic research groups and industrial centers with the facilities necessary for producing state-of-the art GaN material. These involve teams at Strathclyde, Montpellier, Caen, Leuven, Sacavem and Exeter. Grant rates are related to the Marie Curie European scholarship and conditions appropriate for Research Training Networks in Framework V. The opportunities exists for extensive travel between partner sites of the network.

For further details, contact Professor Thomas Frauenheim, or Dr. Ben Hourahine.

frauenheim@phys.uni-paderborn.de
B.Hourahine@phys.uni-paderborn.de
http://www.phys.upb.de/groups/frauenheim/

FB 6 - Theoretische Physik
Universität Paderborn
Warburger Str. 100 D - 33098 Paderborn

PhD Studentship
University of Cambridge, Department of Physics

A 3 year PhD studentship is offered starting in October 2003 in the Theory of Condensed Matter Group at the Physics Department of the University of Cambridge.

The aim is to study the two- and three-dimensional electron-hole gas. The project will involve numerical studies using the quantum Monte Carlo method (see http://www.tcm.phy.cam.ac.uk/ mdt26/cqmc.ht

The studentship is subject to the following application restrictions imposed by the European Commission:

* 35 years or younger at appointment
Non UK Nationals only
EU National or Member of Associated States and not currently based in the UK
see http://www.cordis.lu/fp5/management/ for further details

Enquiries and applications should be sent (preferably by email) to

Professor P B Littlewood
University of Cambridge
Cavendish Laboratory
Madingley Road
Cambridge CB3 0HE, UK
pbl21@phy.cam.ac.uk

The studentship is funded from the Photon-Mediated Phenomena Network, which is a Research Training Network established under the European Commission's Fifth Framework Programme. Started in September 2002 and running for 4 years the network has a commitment to training young researchers in semiconductor opto-electronics and photonics. The network comprises 7 teams from across Europe.

Post-Doctoral Research Assistant in Computer Simulation of Materials

University of Kent, Canterbury, UK

A postdoctoral position is available to work in the newly established Transmanche Centre for Materials Modelling at the University of Kent. The Centre is a multi-national venture supported with EU funding and is a joint project with the universities of Kent, Littoral (Dunkirk) and Picardie (Amiens). The aim of the Centre is to take on materials problems, both academic and technological, using computer simulation methods. The Centre is equipped with a supercomputer and good access to a range of national computing facilities.

For this post we have several challenging projects and we want the successful candidate to have some flexibility in directing the research.

The candidate should have a Ph.D. and experience in computer simulation techniques in chemistry or physics. The emphasis will be on DFT-based electronic structure methods. Knowledge of French would be helpful, but not essential. For more information, contact Dr. Philip Lindan (p.lindan@ukc.ac.uk).

The post is for a two-year period with a possible extension. Closing date for applications: 12 noon Monday 3rd March 2003 Interviews will be held week commencing 17th March 2003 Instructions on the application procedure are at
http://jobs.ac.uk/jobfiles/PD793.html

Positions are available in all three universities and persons who are interested in posts in France should contact Professor Bychkov at Littoral (e-mail; bychkov@hplamer.univ-littoral.fr) or Dr. Rougier at Amiens (e-mail; Aline.Rougier@u-picardie.fr).

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EU-RTN Post-doctoral Position (Louvain-la-Neuve, BELGIUM)

A post-doctoral position, funded by the EU-RTN research network "First-principles approach to the calculation of optical properties of solids" (EXCITING) is available in Louvain-la-Neuve, starting in September-December 2003. Possible topics of the research : - either investigation of the relations between Time-Dependent Density Functional Theory and the Many-Body Perturbation Theory (GW approximation, Bethe-Salpether equation), and their use for the computation of accurate ground-state energy, - or implementation of (new) Time-Dependent (Current) Density functionals, or GW-related functionalities, and their testing.

Eligibility: You must be a national of an EU Member State or Associated State or residing in the Community for at least 5 years prior to the appointment (not a Belgian, though). Maximum age : 35 years (allowance may be made for the actual time spent for military or civil service or child care).

Duration: The position is for 1 year, renewable 1 year.

Qualifications: Candidates should have a PhD and a background in density functional theory and/or many-body perturbation theory.

Application: Applicants should send a CV, a list of publications, and names of two referees to:

Prof. X. Gonze
1, place Croix du Sud
B-1348 Louvain-la-Neuve
BELGIUM
gonze@pcpm.ucl.ac.be
(electronic submission is preferred)

Research Associate in Computational Nanosciences
Université de Montréal, Canada

Applications are invited for an immediate Research Associate (RA) position in the area of computational nanosciences. The position is financed through a grant from NanoQuébec (Québec university network in nanoscience and nanotechnology; http://www.nanoquebec.ca). The RA is expected to provide computational support and participate in the research activities of the various groups active in computational nanosciences on the campus of the Université de Montréal. The candidate will be expected to contribute to code development and implementation, optimization and development of existing codes, data analysis, etc. The ideal candidate possesses extensive experience in computational materials physics and code development; experience with one or several of the following methods is required: electronic structure calculations; ab-initio, density-functional methods; Monte Carlo and kinetic Monte Carlo; empirical and semi-empirical molecular dynamics; activation-relaxation technique; etc.

Interested individuals should send a curriculum vitae, including a list of publications, and the names of three referees, to Prof. Normand Mousseau (Normand.Mousseau@umontreal.ca; `http://www.esi.umontreal.ca/~grofnum`).

Deadline for application is April 1, 2003.

The appointment is for two years: an initial one-year appointment, renewable for a second year upon mutual agreement. Salary is commensurable with experience.

PhD Position in Theoretical Physical Chemistry
Rijksuniversiteit Groningen, Groningen, The Netherlands

A four year PhD-studentship in theoretical physical chemistry is available immediately at the Theoretical Chemistry group of the Rijksuniversiteit Groningen, Groningen, The Netherlands.

FIELDS: theoretical/computational physics/chemistry

KEYWORDS: quantum chemistry, time-dependent (current)-density-functional theory, elementary excitations, response and transport properties, conjugated polymers

SUBJECT: This project is part of a research program that focuses on the new approach of time-dependent current-density-functional theory for calculating excitation and response properties in solid state physics and quantum chemistry. Currently three PhD students and two tenure-track researchers are developing this theoretical and computational method for solids, surfaces, polymers, and large molecules. Jointly with them the successful applicant will study the interplay between electrons and phonons (governing for instance the transport properties in conducting polymers). The derivation of the relevant theory and its implementation in existing computer codes will be needed.

INTERNET: Theoretical Chemistry Group http://theochem.chem.rug.nl, Materials Science Centre: http://www.msc.rug.nl, Rijksuniversiteit Groningen: http://www.rug.nl

APPOINTMENT AND SALARY: The studentship is funded by the Dutch Research Council and is part of a grant for Innovative Research (VIDI). The PhD-student will be appointed for a period of four years with evaluation after one year, and will be offered a monthly salary (before subtraction of taxes and health and social insurance fees, typically 30between Euro 1503 in the first year and Euro 2145 in the fourth year. Additionally, they receive a holiday allowance (8supplement. As part of their training they will be enrolled for courses at international quantum chemistry schools. A course in the Dutch language will also be funded.

QUALIFICATION: Successful candidates should hold a Master in Science, or equivalent degree, in theoretical chemistry or physics, and should be amongst the best of their peer group. They should have good communicative skills and should master the English language. Experience with density functional methods and numerical methods is recommended.

APPLICATION: requests for further information and applications (including a full CV, a list of marks, as well as the summary of the master thesis), and the names and addresses of two academic referees should be sent to dr. ir. Paul L. de Boeij (mailto:p.l.de.boeij@chem.rug.nl) or to prof. dr. Jaap G. Snijders (mailto:j.g.snijders@chem.rug.nl), Theoretical Chemistry, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. Phone:+31.50.363.4375, Fax:+31.50.363.4441. Candidates may be asked to provide a copy of the master thesis. Deadline for submission is May 15 2003, although the search will continue until the post is filled.

Postdoctoral Position in Theoretical and Computational Condensed Matter Physics

in the collaboration of

Feza Gursey Institute/Istanbul and Bilkent University/Ankara, Turkey

Applications are invited for postdoctoral research positions at Feza Gursey Institute in collaboration with the nanostructure group at the Department of Physics, Bilkent University. The areas of research are theoretical and computational studies in nanostructures in the perspective of physical mechanisms for quantum computation. Candidates are expected to be competitive in the areas of electronic structure calculations, and the analytical skills in the areas of quantum coherence-decoherence models and methods.

Successful candidates are expected to work in close collaboration with the nanostructural physics group at Department of Physics, Bilkent University/Ankara (Prof. T. Hakioglu and Prof. O. Gulseren). More information about the department is available at

`http://www.fen.bilkent.edu.tr/~physics` .

Feza Gursey Institute (http://www.gursey.gov.tr) supports basic and applied research in physics and mathematics. The salaries are highly commensurable with the international standards and successful candidates are provided free and furnished on-campus housing (courtesy of Bilkent University). The positions are expected to be for one year and extendable for the second year on mutual agreement and the possibilities for tenure-track academic positions in various Turkish (state and private) Universities may exist.

Interested candidates are invited to submit their CV, list of publications and the contact information of two references to (preferably by e-mail)

Prof. I. H. Duru
Feza Gursey Institute
81220 Cengelkoy, Istanbul
Turkey
e-mail: duru@gursey.gov.tr

(with an e-mail copy to hakioglu@fen.bilkent.edu.tr, or gulseren@fen.bilkent.edu.tr).

PH.D. PROJECT
SIMULATION OF TRANSPORT AND CURRENT-INDUCED MECHANICAL EFFECTS IN ATOMIC-SCALE CONDUCTORS

CONTACT: Tchavdar Todorov and/or Mike Finnis
Atomistic Simulation Group
School of mathematics and Physics
Belfast BT7 1NN, United Kingdom
phone: 028 90335293
email: T.Todorov@qub.ac.uk

1. PAST

We have developed a self-consistent tight-binding formalism to calculate simultaneously:

– the electrical current;
– full interatomic forces in the presence of current flow;
– power dissipation;

in atomic wires under an applied voltage.

2. PRESENT

We are setting up full MD simulations, using the above formalism, to model a current-carrying nanojunction at work.

The MD includes the full forces (zero-voltage forces + current-induced forces) and the power dissipated into the junction by the current.

Our goal is to model dynamically current-induced mechanical effects: local heating, the dynamical effects of current-induced forces and resultant current-induced thermally activated processes, such as current-induced fracture of atomic wires or structural atomistic rearrangements facilitated by the current.

3. FUTURE

We would like to extend the formalism and its implementation in a number of interrelated directions. Each of them, or any combination of them, constitutes a great theme for a fun-packed, innovative Ph.D. study, involving a balance of pen-and-paper theory of atomic-scale conductors and computational work.

These future directions are:

(a) extension of the tight-binding model and its implementation for current-carrying nanoconductors beyond the approximation of local charge neutrality, used at present;

(b) extension of the model to include multiple orbitals, to enable us to model not only simple metallic junctions but also systems such as molecular junctions;

(c) further work on the formal calculation of inelastic corrections to the electronic conductance;

(d) further work on the formal description of electron-phonon coupling, to allow for dynamical screening of the electron-phonon interaction;

(e) anything else that may come up on the way: this is a very fresh field, still in its infancy. Anyone with ideas and a taste for both equations and (relatively simple) computing can have endless fun.

We have links with leading experimentalists in the area. We often look to the latest experiments to give us new problems and new applications.

We expect that a studentship, funded by local government, will be available for a new Ph.D. student, who is a UK national, to take part in this work, starting from next autumn (October 2003).

Please bring this to the attention of anyone interested!

POSTDOCTORAL POSITION

AIST, Tsukuba Advanced Computing Center, Tsukuba, Japan

Applications are invited for a postdoctoral position in computaional nanoscience funded by the "NAtional REsearch Grid Initiative (NAREGI)" project. The position is administered by Prof. K. Terakura at AIST, Tsukuba Advanced Computing Center, Tsukuba, Japan, and the research activity will mainly be conducted under surpervision of Prof. H. Ishida at CHS, Nihon University, Tokyo, Japan. The position is available from June 2003 and its duration is up to 3 years.

The applicant is expected to work in the field of the first-principles studies of the static (ground-state), dynamical, and transport properties of nanostructures, surfaces, and interfaces within the framework of density-functional theory and its extension. This implies applications of the present FLAPW-based computer code as well as further development of the code and basic theory. The applicant should hold a PhD degree or equivalent in physics or chemistry and should have some experience in computational condensed matter theory.

Candidates are asked to send an application letter including a CV, a list of publications, a brief summary of research interests and a letter of recommendation to the following address:

H. Ishida (ishida@chs.nihon-u.ac.jp)

with Cc. to K. Terakura (k-terakura@aist.go.jp).

For more details of the research area, see

1) D. Wortmann, H. Ishida, and S. Bluegel, "An ab initio Green-function formulation of the transfer matrix: Application to complex band structures," PRB65, 165103(2002).

2) D. Wortmann, H. Ishida, and S. Bluegel, "An embedded Green-function approach to the ballistic electron transport through an interface", PRB66, 075113 (2002).

3) H. Ishida and A. Liebsch, "Static and quasi-static response of Ag surfaces to a uniform electric field", Phys. Rev. B66, 155413 (2002).

4) http://zwo.chs.nihon-u.ac.jp (Japanese)

Postdoctoral Positions

Computational Materials Theory Center

California State University Northridge

The Computational Material Theory Center at California State University, Northridge invites applications for several postdoctoral positions available immediately. The research areas include first principles electronic structure calculations and model simulations to study: 1) Dislocation core properties in metals and intermetallics; 2) Strongly Correlated Electron Systems; 3) Electron and spin transport in quantum dots; 4) Electronic and Optical properties of defects and defects reactions in Hydrogen Bonded Molecular Crystals.

The candidate should have experience in ab initio/atomistic methods and/or transport phenomena. The position will be for two years and can be extended for a third year.

Interested candidates should send their resume and two letters of references to

Nicholas Kioussis
Department of Physics and Astronomy
California State University Northridge,
18111 Nordhoff Street, CA 91330-8268
USA

or through email to nick.kioussis@csun.edu.

Open Faculty Positions

TEKNILLINEN KORKEAKOULU
TEKNISKA HÖGSKOLAN
HELSINKI UNIVERSITY OF TECHNOLOGY

Helsinki University of Technology announces the following vacancies:

Department of Materials Science and Rock Engineering

1. Professor in Materials Science (salary class A28) The field of the post is specified to be: Microstructure of Materials, their Mechanical, Electrical, Magnetic and Thermal Properties.

Department of Engineering Physics and Mathematics

2. Professor in Mathematics (salary class A28)

3. Professor in Mathematics (salary class A28)

4. Professor in Engineering Physics (salary class A28) The field of the post is specified to be: Biological Physics

Department of Computer Science and Engineering

5. Professor in Telecommunications Software (salary class A28) The field of the post is specified to be: Communications Software, Especially Application Development in Internet.

Department of Industrial Engineering and Management

6. Professor in Environmental and Quality Management (salary class A28)

7. Professor in Quality Management (salary class A28) The field of the post is specified to be: Especially Quality Engineering, Quality Systems, Quality Improvement or Customer Quality.

Posts 2 and 3: The applicants are presumed to have demonstrated scientific competence especially in the following fields of mathematics: Post 2: Analysis (interpreted widely) or geometry, Post 3 Both stochastic analysis and some central subfield of mathematical analysis.

Posts 6-7 are placed at the local unit of the department and situated in the city of Lahti.

Posts 1-5 will be filled either permanently or at discretion for a certain period, posts 6-7 for a fixed term of five years.

Additional information is available from following persons:

Post 1: Head of Department, Professor Kari Heiskanen tel. +358-9-451 2789 and Administrative Manager Marjukka Petnen tel. +358-9-4512912, fax +358-9-4512899

Post 2: Professor Juhani Pitkranta tel. +358-9-451 3024 and Administrative Manager Katriina Sippola tel. +358-9-451 3000

Post 3: Professor Stig-Olof Londen tel. +358-9-451 3035 and Administrative Manager Katriina Sippola tel. +358-9- 451 3000

Post 4: Professor Risto Nieminen, tel. +358-9-451 3105 and Administrative Manager Katriina Sippola. tel. +358-9- 451 3000

Post 5: Professor Petri Vuorimaa tel. +358-9-451 4794 and Administrative Manager Ilse Koskinen tel. +358-9-451 4800

Posts 6-7: Professor Paul Lillrank, tel. +358-500-703 848 and Professor Ilkka Kauranen tel. +358-3-525 0294 and +358-400-402 310. Email addresses: name.surname@hut.fi.

The particulars of nomination, which contain information about the posts and applying, are available from the Registrar's Office of the University, tel. +358-9-4512030, email kirjaamo@hut.fi. The particulars of nomination can also be read from the HUT website: http://www.hut.fi/avoimet.virat. Particulars of nomination: Post 1, Post 2, Post 3, Post 4, Post 5, Post 6, Post 7.

The applications are to be addressed to the Council of Helsinki University of Technology. The closing date for the applications with appendices is the 16th of April 2003 before 3.45 p.m. The street address of the Registrar's Office is Otakaari 1, Espoo, and the postal address Helsinki University of Technology, P.O.Box 1000, FIN-02015 HUT, Finland.

Espoo, 17th of February 2003
Administrative Office

PHD POSITION IN THEORETICAL CONDENSED MATTER PHYSICS

Physics Department, New Jersey Institute of Technology

A PhD-studentship in theoretical condensed matter physics is available starting fall 2003 at the Physics Department of New Jersey Institute of Technology.

This project is part of a research program that focuses on the new methods for calculating electronic structure, lattice dynamics and electron-phonon couplings in the strongly correlated materials. Successful candidates should hold a Master or equivalent degree in physics. They should have good communicative skills and should master the English language. Experience with numerical methods and programming using Fortran, Java and C++ is highly desired.

The studentship is funded by the National Science Foundation and is a part of NSF Division of Material Research grant. The PhD-student will be appointed for a period of up to total five years with evaluation after one year, and will be offered a competitive salary and benefits.

The New Jersey Institute of Technology is located in downtown Newark with access to the Manhattan area. We have strong collaborations with Rutgers University, Princeton University, Columbia University, and Bell Labs.

Interested candidates should contact S. Savrasov at savrasov@oak.njit.edu.

For additional information, please visit our web site

http://www.njit.edu.

7 Abstracts

Magnetic V embedded in copper evidenced by x-ray magnetic circular dichroism

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M. Teodorescu
Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK
P. Bencok
European Synchrotron Radiation Facility, Grenoble, France
S. S. Dhesi
European Synchrotron Radiation Facility, Grenoble, France

Abstract

We report the observation of a magnetic moment on vanadium embedded in copper. Using x-ray absorption spectroscopy and x-ray magnetic circular dichroism we show that the vanadium atomic magnetic moment is strongly dependent on the formation temperature of the VCu alloy. The absorption spectra allow us to distinguish the electronic transitions which are the signature of the magnetic state from the non magnetic states. We discuss the temperature dependence of the magnetic moment of vanadium and show that alloys prepared at 250 K and 270 K do follow a ferrimagnetic behavior rather than a Curie-Weiss law.

(Phys. Rev. B, 1 March, 2003)
Contact person: g.vanderlaan@dl.ac.uk

Sum rules in x-ray resonant Raman scattering: recovering Co ground state information in $CoFe_2O_4$ as a test case

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Piazza Leonardo da Vinci 32, 20122 Milano, Italy
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N.B. Brookes
ESRF, European Synchrotron Radiation Facility, B.P. 220,
F-38043 Grenoble Cedex, France

Abstract

We present an approach to x-ray resonant Raman scattering suitable for sum-rule analysis. In magnetic systems it gives ground-state information as represented by an expansion in coupled multipoles of orbital and spin moments. The experiment is based on the angular dependence of the integrated peak intensities. In $3d$ transition elements one obtains information up to order four from the channel $2p^6 3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 2p^6 3s^1 3d^{n+1}$. By combining these results with $L_{2,3}$ absorption dichroism, we show quantitatively the atomic-like properties of cobalt in $CoFe_2O_4$ up to high order multipoles.

(Physical Review Letters, accepted)
Contact person: g.vanderlaan@dl.ac.uk

Photovoltage detection of x-ray absorption and magnetic circular dichroism spectra of magnetic films grown on semiconductors

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H.K. Tsang
Chinese University of Hong Kong, Department of Electrical Engineering,
Shatin, Hong Kong, Peoples Republic of China
G. van der Laan
Daresbury Laboratory, Warrington WA4 4AD, Cheshire, England

Abstract

We describe a measurement technique for x-ray absorption spectroscopy, in which the sample is used as the detector. Co L_2, L_3 absorption spectra were taken from cobalt films grown on n-GaAs by measuring the photovoltage generated by the x rays transmitted across the rectifying metal-semiconductor contact. After correcting the effects of signal saturation good agreement was obtained with spectra acquired using the conventional total electron yield method. X-ray magnetic circular dichroism measurements using the method gave values for the spin moment of cobalt between 1.48 and 1.89 μ_B/atom, compared to the value in the literature of 1.55 μ_B/atom for the bulk. An anomalously high average value of 0.39 μ_B/atom was found for the orbital moment and attributed to the presence of oxide in the films.

(Published in JOURNAL OF APPLIED PHYSICS 93 (4): 2028-2033 FEB 15 2003)
Claim your free reprint today by emailing: g.vanderlaan@dl.ac.uk

Site exchange in ultrathin layers of Ni on Cu(100) studied with element-specific layer-by-layer resolution

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Daresbury Laboratory, Warrington, WA4 4AD, UK
P. Bailey
Daresbury Laboratory, Warrington, WA4 4AD, UK
G. van der Laan
Daresbury Laboratory, Warrington, WA4 4AD, UK

Abstract

We use medium energy ion scattering to determine the composition of each of the topmost three atomic layers of a single crystal of copper coated with an epitaxial sub-monolayer of nickel as a function of anneal temperature in the range 140 to 420 K. The technique confers layer and elemental resolution even though the constituents are adjacent in the periodic table. At a transition temperature of around 300 K, sub-surface copper and surface nickel interchange so that the nickel comes to reside almost exclusively in the sub-surface layer and the top layer of the crystal becomes almost purely copper. Implications of the result for magnetic measurements are briefly sketched.

(Accepted for publication in Phys. Rev. B)
Contact person: g.vanderlaan@dl.ac.uk

Hafnium Nitride, Hf_3N_4, with Thorium Phosphide Structure: Physical Properties and an Assessment of the Hf-N, Zr-N, and Ti-N Phase Diagrams at High Pressures and Temperatures

Peter Kroll
Institut für Anorganische Chemie,
Rheinisch-Westfälische Technische Hochschule Aachen (RWTH),
Professor-Pirlet-Strasse 1, 52056 Aachen, Germany

Abstract

The physical properties of the new cubic phase of Hf_3N_4 as well as of isomorphic Zr_3N_4 and Ti_3N_4 are studied using first-principles calculations. Hf_3N_4, Zr_3N_4, and Ti_3N_4 are semiconductors with band gaps of 1.8, 1.1, and 0.6 eV, respectively. The band structure is characterized by the simultaneous presence of steep and extremly flat bands. The calculated shear modulus G indicates that the cubic Hf_3N_4 will be slightly harder than the mononitride HfN. Under ambient conditions, the cubic modifications of M_3N_4 (M=Hf,Zr,Ti) are metastable with respect to orthorhombic M_3N_4 phases, but the orthorhombic phases of Hf_3N_4 and Zr_3N_4 are stable with respect to the mononitrides and nitrogen. We predict the synthesis at 2800 K of cubic phases of Zr_3N_4 and Ti_3N_4 at 45 GPa and 100 GPa, respectively.

(PRL accepted Feb 5 2002)
Preprint available by request from the author: peter.kroll@ac.rwth-aachen.de

Ab initio study of charge order in Fe_3O_4

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DK-8000 Aarhus C, Denmark
[3] *Metals and Ceramics Division, Oak Ridge National Laboratory,*
Oak Ridge, TN, USA
[4] *INFP, Forschungszentrum Karlsruhe GmbH, Postfach 3640,*
D-76021 Karlsruhe, Germany

Abstract

We present a self-interaction corrected local spin density (SIC-LSD) study of the electronic structure and possible charge order of magnetite, Fe_3O_4. The issue of charge order in magnetite is explored in both cubic and orthorhombic structures, the latter being an approximation to the true, low temperature, monoclinic structure. We find that the Verwey charge ordered phase is not the groundstate solution for this compound neither in cubic nor orthorhombic structure.

(cond-mat/0302229)
Contact person: Z.Szotek@dl.ac.uk

Electronic structure of half-metallic double perovskites

Z. Szotek[1], W.M. Temmerman[1], A. Svane[2], L. Petit[2], and H. Winter[3]
[1] *Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U.K.*
[2] *Institute of Physics and Astronomy, University of Aarhus,*
DK-8000 Aarhus C, Denmark
[3] *INFP, Forschungszentrum Karlsruhe GmbH, Postfach 3640,*
D-76021 Karlsruhe, Germany

Abstract

We present the self-interaction corrected local spin density (SIC-LSD) electronic structure and total energy calculations, leading also to valencies of the ground state configurations, for the half-metallic double perovskites such as Sr_2FeMoO_6, Ba_2FeMoO_6, Ca_2FeMoO_6, and Ca_2FeReO_6. We conclude that the Fe and Mo (or Re) spin magnetic moments are anti-parallel aligned, and the magnitude of the hybridization induced moment on Mo does not vary much between the different compounds. The hybridization spin magnetic moment on Re is of the order of -1.1 μ_B, while that on Mo is about -0.4 μ_B, independently of the alkaline earth element. Also the electronic structure of all the compounds studied is very similar, with a well defined gap in the majority spin component and metallic density of states for the minority spin component, with highly hybridized Fe, Mo (or Re), and oxygen bands.

(cond-mat/0302360)
Contact person: Z.Szotek@dl.ac.uk

The Korringa-Kohn-Rostoker Non-Local Coherent Potential Approximation (KKR-NLCPA)

D.A.Rowlands
Dept. of Physics, University of Warwick, Coventry CV4 7AL, U.K.
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B.L.Györffy
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Abstract

We introduce the Korringa-Kohn-Rostocker non-local coherent potential approximation (KKR-NLCPA) for describing the electronic structure of disordered systems. The KKR-NLCPA systematically provides a hierarchy of improvements upon the widely used KKR-CPA approach and includes non-local correlations in the disorder configurations by means of a self-consistently embedded cluster. The KKR-NLCPA method satisfies all of the requirements for a successful cluster generalization of the KKR-CPA; it remains fully causal, becomes exact in the limit of large cluster sizes, reduces to the KKR-CPA for a single-site cluster, is straightforward to implement numerically, and enables the effects of short-range order upon the electronic structure to be investigated. In particular, it is suitable for combination with electronic density functional theory to give an ab-initio description of disordered systems. Future applications to charge correlation and lattice displacement effects in alloys and spin fluctuations in magnets amongst others are very promising. We illustrate the method by application to a simple one-dimensional model.

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Prediction of a new class of half-metallic antiferromagnets

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Abstract

We report on vacancy induced half-metallicity in the prototype Mott-insulating substances MnO and NiO. By embedding a cation-vacancy into a *magnetic* system a new road opens up to the construction of half-metallic antiferromagnets. For $Ni_{0.97}O$ we find a half-metallic antiferromagnet a system hitherto only proposed for complicated crystal structures.

(cond-mat/0303354)

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Ab initio charge, spin and orbital energy scales in $LaMnO_3$

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Abstract

The first-principles SIC-LSD theory is utilized to study electronic, magnetic and orbital phenomena in $LaMnO_3$. The correct ground state is found, which is antiferro orbitally ordered with the spin magnetic moments antiferromagnetically aligned. Jahn-Teller energies are found to be the largest energy scale. In addition it is the Jahn-Teller interaction which is the dominant effect in realising orbital order, and the electronic effects alone do not suffice.

(cond-mat/0303602)

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Composition and structure of the $RuO_2(110)$ surface in an O_2 and CO environment: Implications for the catalytic formation of CO_2

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Abstract

The phase diagram of surface structures for the model catalyst $RuO_2(110)$ in contact with a gas environment of O_2 and CO is calculated by density-functional theory and atomistic thermodynamics. Adsorption of the reactants is found to depend crucially on temperature and partial pressures in the gas phase. Assuming that a catalyst surface under steady-state operation conditions is close to a constrained thermodynamic equilibrium, we are able to rationalize a number of experimental findings on the CO oxidation over $RuO_2(110)$. We also calculated reaction pathways and energy barriers. Based on the various results the importance of phase coexistence conditions is emphasized as these will lead to an enhanced dynamics at the catalyst surface. Such conditions may actuate an additional, kinetically controlled reaction mechanism on $RuO_2(110)$.

(submitted to: Phys. Rev. B)
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8 Presenting Other Initiatives

8.1 New Release of the PWscf package

A new version (1.2.0) of the PWscf package is available for download on the web site http://www.pwscf.org.

The new version contains many changes, improvements, bug fixes. Everybody who is using the PWscf package is encouraged to upgrade and to report problems to the mailing list. Those who do not yet know PWscf are invited to give it a try.

This release is the first step of a project aiming at a full integration and interoperability of PWscf with the Car-Parrinello codes FPMD (Cineca Bologna and Sissa Trieste) and CP (IRRMA Lausanne and Princeton University), recently released under the GNU license, soon available for download from the web site http://www.democritos.it

Major changes:

- faster iteration to self-consistently (if you find a case in which this is not true, please let us know)
- (much) better format for input data
- a new unified pseudopotential file (UPF) has been introduced; old formats are still recognized, but we strongly encourage to convert pseudopotential files using the converters provided with the code
- new output data file format (this is invisible to users)
- calculation of dielectric tensor with ultrasoft pseudopotentials (experimental)
- faster scf and phonon calculation when using Gamma point only (experimental)
- a GUI (Graphical User Interface) for input data is available as a separate package (experimental, contributed by Tone Kokalj)
- a new unified pseudopotential file (UPF) has been introduced; old formats are still recognized, but we strongly encourage to convert pseudopotential files using the converters provided with the code.

Note that both the directory structure of the package and the installation mechanism has changed a bit. New examples with the new input data structure are available.

The PWscf group

9 SCIENTIFIC HIGHLIGHT OF THE MONTH

Realistic investigations of correlated electron systems with LDA+DMFT

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Abstract

Conventional band structure calculations in the local density approximation (LDA)[1–3] are highly successful for many materials, but miss important aspects of the physics and energetics of strongly correlated electron systems, such as transition metal oxides and f-electron systems displaying, e.g., Mott insulating and heavy quasiparticle behavior. In this respect, the LDA+DMFT approach which merges LDA with a modern many-body approach, the dynamical mean-field theory (DMFT) has proved to be a breakthrough for the realistic modeling of correlated materials. Depending on the strength of the electronic correlation, a LDA+DMFT calculation yields the weakly correlated LDA results, a strongly correlated metal, or a Mott insulator. In this paper, the basic ideas and the set-up of the LDA+DMFT(X) approach, where X is the method used to solve the DMFT equations, are discussed. Results obtained with X=QMC (quantum Monte Carlo) and X=NCA (non-crossing approximation) are presented and compared, showing that the method X matters quantitatively. We also discuss LDA+DMFT results for two prime examples of correlated materials, i.e., V_2O_3 and Ce which undergo a Mott-Hubbard metal-insulator and volume collapse transition, respectively.

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1 Introduction

One of the most important challenges of theoretical solid state physics is the development of tools for the accurate calculation of material properties. In this respect, density functional theory (DFT) within the local density approximation (LDA)[1–3] turned out to be unexpectedly successful, and established itself as *the* method for realistic solid state calculations in the last century. This is surprising because LDA is a serious approximation to the Coulomb interaction between electrons. In particular the correlation but also the exchange contribution of the Coulomb interaction is only treated rudimentarily, i.e., by means of a *local* density and by a functional obtained from the jellium model, a weakly correlated problem. The success of LDA shows, however, that this treatment is sufficient for many materials, both for calculating ground state energies and bandstructures, implying that electronic correlations are rather weak in these materials. However, there are important classes of materials where LDA fails, such as transition metal oxides or heavy fermion systems, i.e., materials where electronic correlations are strong. For example, LDA predicts La_2CuO_4 and V_2O_3, to be metals[4,5] whereas, in reality, they are insulators. The physics of these Mott insulators is dominated by the formation of Hubbard bands, an effect of electronic correlations which splits the LDA bands into two sets of bands, separated by a local Coulomb repulsion U. Such Mott insulating behavior occurs already in the paramagnetic phase, with magnetic order setting in at lower temperatures. The Mott physics and the associated energy gain is completely missing in the LDA. It can, however, be described by the LDA+U method, at least for ordered systems. But, the energy gain due to the formation of Hubbard bands is so large in LDA+U that for realistic values of U it almost automatically yields split bands and (ordered) insulating behavior, even if this is not correct. The reason for this is that the energy of the correlated metal is strongly overestimated. Hence, LDA+U is a

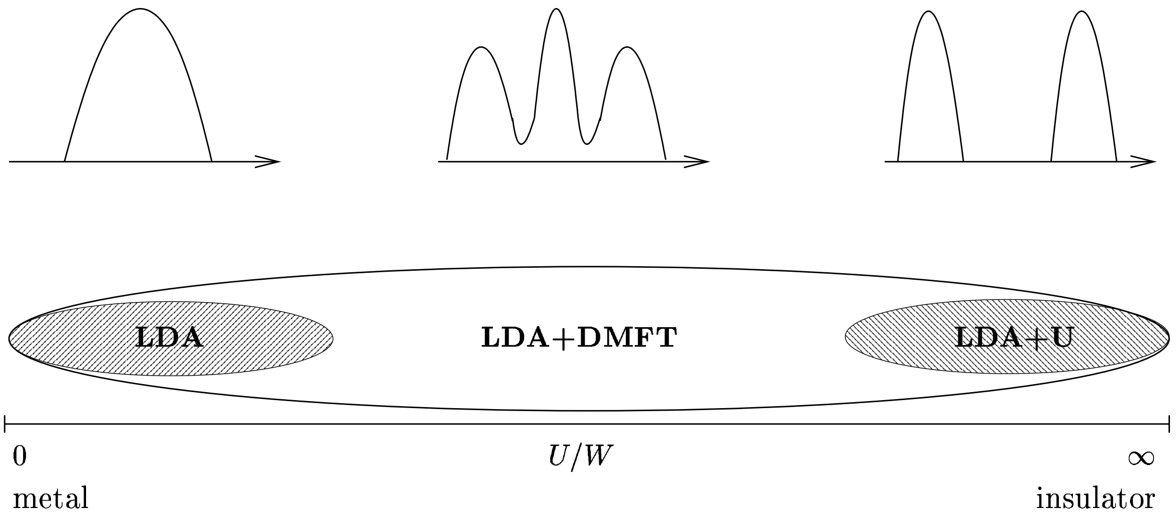


Figure 1: With increasing strength of the local Coulomb repulsion U (relative to the LDA bandwidth W), one observes a weakly correlated metal (left density of states), a strongly correlated metal with a quasiparticle peak at the Fermi energy (middle), and a Mott insulator (right). The weakly correlated metal and the (ordered) Mott insulator are correctly described by LDA and LDA+U, respectively. LDA+DMFT gives the correct answer for all values of U and subsumes the LDA valid for small U/W and the LDA+U results for the Mott insulator appearing at large U/W.

good method for describing Mott insulators, but not for calculating strongly correlated metals or systems in the vicinity of a Mott-Hubbard metal-insulator transition. Missing in both LDA and LDA+U is the *quasiparticle physics*, which even at a rather large Coulomb interaction U (or at $U = \infty$ with a non-integer number of interacting electrons per site) still gives a metallic behavior determined by quasiparticles with a larger effective mass than the LDA electrons. This mass enhancement ranges from a moderate increase in many transition metal oxides to the high effective masses observed in $4f$-based heavy fermion compounds. LDA and also LDA+U fail to account for this kind of physics and the associated Kondo-like energy scale gained in comparison with the Mott insulator.

LDA+DMFT does not only include the correct quasiparticle physics and the corresponding energetics but, at the same time, reproduces the LDA and LDA+U results in the limits where these methods are valid, see Fig. 1. For weakly correlated systems, we know that LDA provides the correct description, as does the LDA+DMFT approach which gives the same results as LDA if the local Coulomb interaction U is small. On the other hand, LDA+DMFT agrees with the LDA+U results for symmetry-broken Mott insulators at large Coulomb interaction U. In addition, however, LDA+DMFT also describes the correlated metals occurring either at somewhat smaller Coulomb interactions U *or* when Mott insulators are doped. Thus, LDA+DMFT provides the correct physics for all Coulomb interactions and dopings, whereas LDA yields an uncorrelated metal even if the material at hand is a strongly-correlated metal or a Mott insulator. Similarly, LDA+U yields an insulator for the *ab-initio*-calculated U-values of 3d transition metal oxides, even for materials which should be metallic.

With the ability of LDA+DMFT to describe the full range of materials from weakly to strongly correlated metals to Mott insulators, it is not astonishing that it has proved to be a breakthrough for the calculation of correlated materials. Since more and more physicists from the bandstructure and many-body communities show interest in this novel method, we would like to present here, as a ψ_k scientific highlight of the month, an introduction to LDA+DMFT. We also present results for two of the most famous strongly-correlated materials, i.e., the transition metal oxide V_2O_3 which is the prime example of a system undergoing a Mott-Hubbard metal-insulator transition, and the $4f$-electron system Ce with its volume collapse transition. The presentation is following in many parts the conference proceedings Ref. 6, also see the conference proceedings Refs. 7.

In Section 2 the LDA+DMFT approach is presented, starting with the *ab initio* electronic Hamiltonian in Section 2.1, continuing with DFT in Section 2.2, LDA in Section 2.3, the construction of a model Hamiltonian in Section 2.4, and DMFT in Section 2.5. As methods used to solve the DMFT we discuss the quantum Monte Carlo (QMC) algorithm in Section 2.6 and the non-crossing approximation (NCA) in Section 2.7. A simplified treatment for transition metal oxides is introduced in Section 2.8. Extensions and alternatives to the LDA+DMFT approach are discussed, focusing on a self-consistent LDA+DMFT scheme in Section 3.1, spectral density functional theory in Section 3.2, cluster extensions of DMFT in Section 3.3, and the GW+DMFT approach in Section 3.4. As a particular example, the LDA+DMFT calculation for $La_{1-x}Sr_xTiO_3$ is discussed in Section 4, emphasizing that the method X to solve the DMFT matters on a quantitative level. Our calculations for the Mott-Hubbard metal-insulator transition in V_2O_3 are presented in Section 5, in comparison to the experiment. Section 6 reviews our recent calculations of the Ce α-γ transition, in the perspective of the models referred to as Kondo volume collapse and Mott transition scenario. A summary of the LDA+DMFT set-up and applications followed by a discussion of future prospects closes the presentation in Section 7.

2 The LDA+DMFT approach

2.1 Ab initio electronic Hamiltonian

Within Born-Oppenheimer approximation[8] and neglecting relativistic effects, electronic properties of solid state systems are described by the electronic Hamiltonian

$$\begin{aligned}\hat{H} \;=\;& \sum_{\sigma} \int d^3r\; \hat{\Psi}^+(\mathbf{r},\sigma) \left[-\frac{\hbar^2}{2m_e}\Delta + V_{\text{ion}}(\mathbf{r}) \right] \hat{\Psi}(\mathbf{r},\sigma) \\ &+ \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r\, d^3r'\; \hat{\Psi}^+(\mathbf{r},\sigma)\hat{\Psi}^+(\mathbf{r}',\sigma')\; V_{\text{ee}}(\mathbf{r}-\mathbf{r}')\; \hat{\Psi}(\mathbf{r}',\sigma')\hat{\Psi}(\mathbf{r},\sigma). \qquad (1)\end{aligned}$$

Here, $\hat{\Psi}^+(\mathbf{r},\sigma)$ and $\hat{\Psi}(\mathbf{r},\sigma)$ are field operators that create and annihilate an electron at position $\mathbf{r}$ with spin σ, Δ is the Laplace operator, m_e the electron mass, e the electron charge, and

$$V_{\text{ion}}(\mathbf{r}) = -e^2 \sum_i \frac{Z_i}{|\mathbf{r}-\mathbf{R_i}|} \quad \text{and} \quad V_{\text{ee}}(\mathbf{r}-\mathbf{r}') = \frac{e^2}{2} \sum_{\mathbf{r}\neq\mathbf{r}'} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \qquad (2)$$

denote the one-particle ionic potential of all ions i with charge eZ_i at given positions $\mathbf{R_i}$, and the electron-electron interaction, respectively.

While the *ab initio* Hamiltonian (1) is easy to write down it is impossible to solve it exactly if more than a few electrons are involved. Numerical methods like Green's Function Monte Carlo and related approaches have been used successfully for relatively modest numbers of electrons. Even so, however, the focus of the work has been on jellium and on light atoms and molecules like H, H_2, ^{3}He, ^{4}He with only a few electrons. Because of this, one has to make substantial approximations to deal with the Hamiltonian (1) like the LDA approximation or the LDA+DMFT approach which is the subject of the present paper.

2.2 Density functional theory

The fundamental theorem of DFT by Hohenberg and Kohn[1] (see, e.g., the review by Jones and Gunnarsson[3]) states that the ground state energy is a functional of the electron density which assumes its minimum at the electron density of the ground state. Following Levy,[9] this theorem is easily proved and the functional even constructed by taking the minimum (infimum) of the energy expectation value w.r.t. all (many-body) wave functions $\varphi(\mathbf{r_1}\sigma_1, \ldots \mathbf{r_N}\sigma_N)$ at a given electron number N which yield the electron density $\rho(\mathbf{r})$:

$$E[\rho] = \inf\Big\{\langle\varphi|\hat{H}|\varphi\rangle \;\Big|\; \langle\varphi|\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r_i})|\varphi\rangle = \rho(\mathbf{r})\Big\}. \tag{3}$$

However, this construction is of no practical value since it actually requires the evaluation of the Hamiltonian (1). Only certain contributions like the Hartree energy, i.e., $E_{\text{Hartree}}[\rho] = \frac{1}{2}\int d^3r'\, d^3r\; V_{\text{ee}}(\mathbf{r}{-}\mathbf{r}')\;\rho(\mathbf{r}')\rho(\mathbf{r})$, and the energy of the ionic potential $E_{\text{ion}}[\rho] = \int d^3r\; V_{\text{ion}}(\mathbf{r})\;\rho(\mathbf{r})$ can be expressed directly in terms of the electron density. This leads to

$$E[\rho] = E_{\text{kin}}[\rho] + E_{\text{ion}}[\rho] + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho], \tag{4}$$

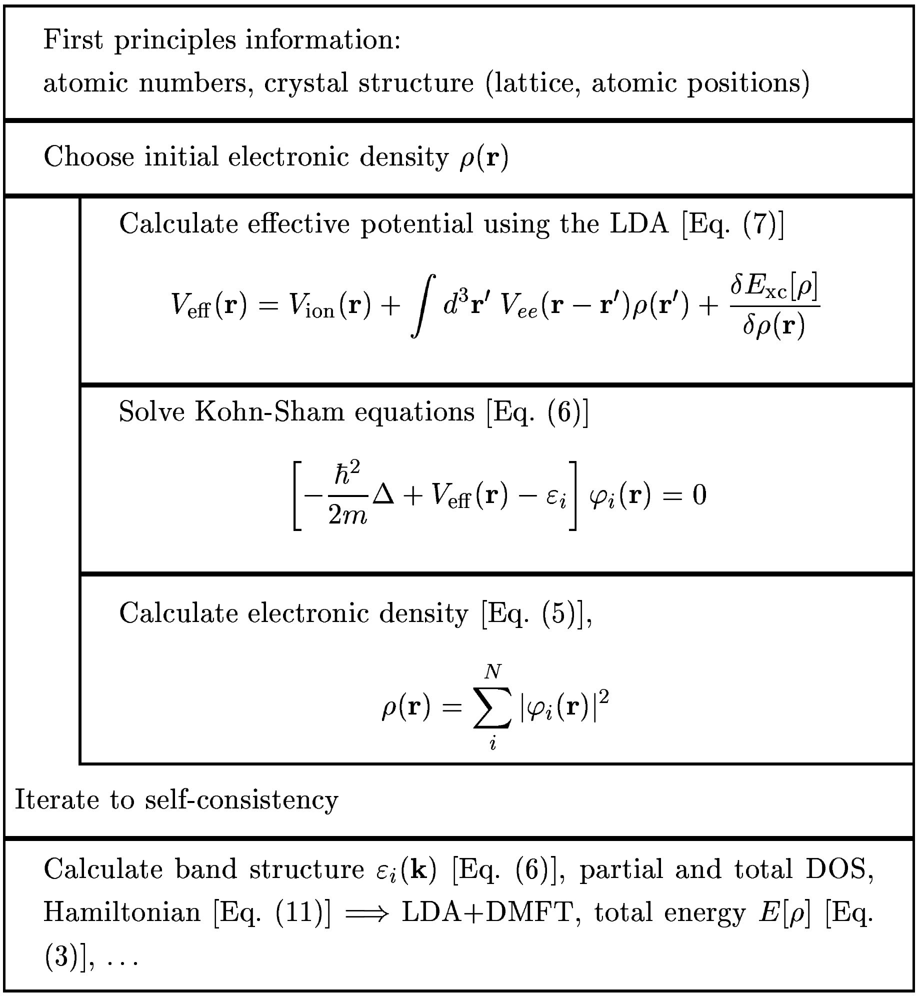
where $E_{\text{kin}}[\rho]$ denotes the kinetic energy, and $E_{\text{xc}}[\rho]$ is the unknown exchange and correlation term which contains the energy of the electron-electron interaction except for the Hartree term. Hence all the difficulties of the many-body problem have been transferred into $E_{\text{xc}}[\rho]$. Instead of minimizing $E[\rho]$ with respect to ρ one minimizes it w.r.t. a set of one-particle wave functions φ_i related to ρ via

$$\rho(\mathbf{r}) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2. \tag{5}$$

To guarantee the normalization of φ_i, the Lagrange parameters ε_i are introduced such that the variation $\delta\{E[\rho] + \varepsilon_i[1 - \int d^3r|\varphi_i(\mathbf{r})|^2]\}/\delta\varphi_i(\mathbf{r}) = 0$ yields the Kohn-Sham[2] equations:

$$\left[-\frac{\hbar^2}{2m_e}\Delta + V_{\text{ion}}(\mathbf{r}) + \int d^3r'\; V_{\text{ee}}(\mathbf{r}{-}\mathbf{r}')\rho(\mathbf{r}') + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}\right]\varphi_i(\mathbf{r}) = \varepsilon_i\;\varphi_i(\mathbf{r}). \tag{6}$$

These equations have the same form as a one-particle Schrödinger equation and yield a kinetic energy for the one-particle wave-function ansatz, i.e., $E_{\text{kin}}[\rho_{\text{min}}] = -\sum_{i=1}^{N}\langle\varphi_i|\hbar^2\Delta/(2m_e)|\varphi_i\rangle$ where φ_i denote the self-consistent (spin-degenerate) solutions of Eqs. (6) and (5) with lowest "energy" ϵ_i. However, this kinetic energy functional gives not the true kinetic energy of the



First principles information:
atomic numbers, crystal structure (lattice, atomic positions)

Choose initial electronic density $\rho(\mathbf{r})$

Calculate effective potential using the LDA [Eq. (7)]

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int d^3\mathbf{r}'\, V_{ee}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

Solve Kohn-Sham equations [Eq. (6)]

$$\left[-\frac{\hbar^2}{2m}\Delta + V_{\text{eff}}(\mathbf{r}) - \varepsilon_i\right]\varphi_i(\mathbf{r}) = 0$$

Calculate electronic density [Eq. (5)],

$$\rho(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2$$

Iterate to self-consistency

Calculate band structure $\varepsilon_i(\mathbf{k})$ [Eq. (6)], partial and total DOS, Hamiltonian [Eq. (11)] $\Longrightarrow$ LDA+DMFT, total energy $E[\rho]$ [Eq. (3)], ...

Figure 2: Flow diagram of the DFT/LDA calculations.

correlated problem which would require that the exact δE_{xc} also comprises the difference. Also note, that the one-particle potential of Eq. (6), i.e.,

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int d^3r'\, V_{\text{ee}}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{7}$$

is only an auxiliary potential which artificially arises in the approach to minimize $E[\rho]$. Thus, the wave functions φ_i and the Lagrange parameters ε_i have no physical meaning at this point. Altogether, these equations allow for the DFT/LDA calculation, see the flow diagram Fig. 2.

2.3 Local density approximation

So far no approximations have been employed since the difficulty of the many-body problem was only transferred to the unknown functional $E_{\text{xc}}[\rho]$. For this term the local density approximation (LDA) which approximates the functional $E_{\text{xc}}[\rho]$ by a function that depends on the local density only, i.e.,

$$E_{\text{xc}}[\rho] \to \int d^3r\, E_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r})), \tag{8}$$

was found to be unexpectedly successful. Here, $E_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r}))$ is usually calculated from the perturbative solution[10] or the numerical simulation[11] of the jellium problem which is defined by

$V_{\rm ion}(\mathbf{r}) = \text{const.}$

In principle, DFT/LDA only allows one to calculate static properties like the ground state energy or its derivatives. However, one of the major applications of LDA is the calculation of band structures. To this end, the Lagrange parameters ε_i *are interpreted* as the physical (one-particle) energies of the system under consideration. Since the true ground-state is not a simple one-particle wave-function, this is an approximation beyond DFT. Actually, this approximation corresponds to the replacement of the Hamiltonian (1) by

$$\hat{H}_{\rm LDA} = \sum_\sigma \int d^3r \; \hat{\Psi}^+(\mathbf{r},\sigma) \left[\frac{-\hbar^2}{2m_e}\Delta + V_{\rm ion}(\mathbf{r}) + \int d^3r' \, V_{\rm ee}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \frac{\delta E_{\rm xc}^{\rm LDA}[\rho]}{\delta\rho(\mathbf{r})} \right] \hat{\Psi}(\mathbf{r},\sigma). \quad (9)$$

For practical calculations one needs to expand the field operators w.r.t. a basis Φ_{ilm}, e.g., a linearized muffin-tin orbital (LMTO)[12,13] basis (i denotes lattice sites; l and m are orbital indices). In this basis,

$$\hat{\Psi}^+(\mathbf{r},\sigma) \;=\; \sum_{ilm} \hat{c}_{ilm}^{\sigma\dagger} \Phi_{ilm}(\mathbf{r}) \qquad (10)$$

such that the Hamiltonian (9) reads

$$\hat{H}_{\rm LDA} \;=\; \sum_{ilm,jl'm',\sigma} (\delta_{ilm,jl'm'} \, \varepsilon_{ilm} \; \hat{n}_{ilm}^\sigma + t_{ilm,jl'm'} \; \hat{c}_{ilm}^{\sigma\dagger} \hat{c}_{jl'm'}^\sigma). \qquad (11)$$

Here, $\hat{n}_{ilm}^\sigma = \hat{c}_{ilm}^{\sigma\dagger} \hat{c}_{ilm}^\sigma$,

$$t_{ilm,jl'm'} = \left\langle \Phi_{ilm} \middle| -\frac{\hbar^2\Delta}{2m_e} + V_{\rm ion}(\mathbf{r}) + \int d^3r' V_{\rm ee}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \frac{\delta E_{\rm xc}^{\rm LDA}[\rho]}{\delta\rho(\mathbf{r})} \middle| \Phi_{jl'm'} \right\rangle \qquad (12)$$

for $ilm \neq jl'm'$ and zero otherwise; ε_{ilm} denotes the corresponding diagonal part.

As for static properties, the LDA approach based on the self-consistent solution of Hamiltonian (11) together with the calculation of the electronic density Eq. (5) [see the flow diagram Fig. 2] has also been highly successful for band structure calculations – but only for weakly correlated materials.[3] It is not reliable when applied to correlated materials and can even be completely wrong because it treats electronic *correlations* only very rudimentarily.

2.4 Supplementing LDA with local Coulomb correlations

Of prime importance for correlated materials are the local Coulomb interactions between d- and f-electrons on the same lattice site since these contributions are largest. This is due to the extensive overlap (w.r.t. the Coulomb interaction) of these localized orbitals which results in strong correlations. Moreover, the largest non-local contribution is the nearest-neighbor density-density interaction which, to leading order in the number of nearest-neighbor sites, yields only the Hartree term (see Ref. 14 and, also, Ref. 15) which is already included in the LDA. To take the local Coulomb interactions into account, one can supplement the LDA Hamiltonian (11) with the local Coulomb matrix approximated by the (most important) matrix elements $U_{mm'}^{\sigma\sigma'}$ (Coulomb repulsion and Z-component of Hund's rule coupling) and $J_{mm'}$ (spin-flip terms of Hund's rule coupling) between the localized electrons (for which we assume $i = i_d$ and $l = l_d$):

$$\hat{H} \;=\; \hat{H}_{\rm LDA} + \frac{1}{2} \sum_{i=i_d,l=l_d} \sum_{m\sigma,m'\sigma'}{}' \; U_{mm'}^{\sigma\sigma'} \hat{n}_{ilm\sigma} \hat{n}_{ilm'\sigma'}$$

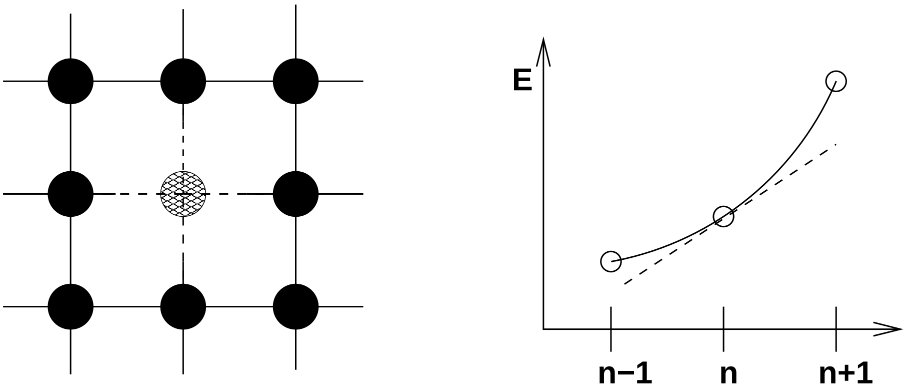


Figure 3: Left: In the constrained LDA calculation the interacting *d*- or *f*-electrons on one lattice site are kinetically decoupled from the rest of the system, i.e., they cannot hop to other lattice sites or to other orbitals. By contrast, the *non*-interacting electrons can still still hop to other sites (indicated by dashed lines). Right: This allows one to constrain the number n of interacting *d*- or *f*-electrons on the decoupled site and to calculate the corresponding LDA energies $E(n)$ (circles); the dashed line sketches the behavior of $\hat{H}_{\text{LDA}}$ defined in Eq. (11).

$$-\frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'}{}' J_{mm'}\hat{c}^{\dagger}_{ilm\sigma}\hat{c}^{\dagger}_{ilm'\bar{\sigma}}\hat{c}_{ilm'\sigma}\hat{c}_{ilm\bar{\sigma}} - \sum_{i=i_d,l=l_d}\sum_{m\sigma}\Delta\epsilon_d\,\hat{n}_{ilm\sigma}. \tag{13}$$

Here, the prime on the sum indicates that at least two of the indices of an operator have to be different, and $\bar{\sigma} =\downarrow (\uparrow)$ for $\sigma =\uparrow (\downarrow)$. In principle, also a pair hopping term of the form $\frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'}' J_{mm'}\hat{c}^{\dagger}_{ilm\sigma}\hat{c}^{\dagger}_{ilm\bar{\sigma}}\hat{c}_{ilm'\sigma}\hat{c}_{ilm'\bar{\sigma}}$ would occur in Eq. (13). This term has not yet been included in LDA+DMFT calculations because one commonly assumes that configurations where one orbital is doubly occupied while another is empty are rare if the Hund's exchange and the hopping terms are included. In typical applications we have $U^{\uparrow\downarrow}_{mm} \equiv U$, $J_{mm'} \equiv J$, $U^{\sigma\sigma'}_{mm'} = U - 2J - J\delta_{\sigma\sigma'}$ for $m \neq m'$ (here, the first term $2J$ is due to the reduced Coulomb repulsion between different orbitals and the second term $J\delta_{\sigma\sigma'}$ directly arises from the Z-component of Hund's rule coupling). With the number of interacting orbitals M, the average Coulomb interaction is then

$$\bar{U} = \frac{U + (M-1)(U-2J) + (M-1)(U-3J)}{2M-1}. \tag{14}$$

The last term of the Hamiltonian (13) reflects a shift of the one-particle potential of the interacting orbitals and is necessary if the Coulomb interaction is taken into account. This last term led to some criticism and we would, thus, like to discuss the origin of this term in more detail below.

The calculation of the local Coulomb interaction $\bar{U}$, or similarly the Hund's exchange constant J, is not at all trivial and requires additional approximations. Presently, the best method available which takes into account screening effects is the constrained LDA method.[16] The basic idea of constrained LDA is to perform LDA calculations for a slightly modified problem, i.e., a problem where the interacting *d*- or *f*-electrons of one site are kinetically decoupled from the rest of the system, i.e., their hopping matrix elements $t_{il_dm,jlm'}$ are set to zero, see Fig. 3. This allows one to change the number of interacting electrons on this site. At the same time screening effects of the other electrons, which are redistributed if the number of *d*- or *f*-electrons is changed on the decoupled site, are taken into account. In a LDA+DMFT calculation, one expects an average number n_d of interacting electrons per site on average; typically n_d is close to an integer number. Then, one can do constrained LDA calculations for $n-1$, n, and $n+1$ electrons on the decoupled site, leading to three corresponding total energies, see Fig. 3. The LDA Hamiltonian $\hat{H}_{\rm LDA}$ which was calculated at a fixed density $\rho(r)$ would predict a linear change of the LDA energy with the number of interacting electrons, i.e., $E(n_d) = E_0 + \epsilon_d^{\rm LDA}\, n_d$ with $\epsilon_d^{\rm LDA} = dE^{\rm LDA}/dn_d$. This does not take into account the Coulomb interaction $\bar{U}$ which requires a higher energy cost to add the $(n+1)$th electron than to add the nth electron. This effect leads to the curvature in Fig. 3 and is taken into account in the Hamiltonian (13) which yields $E(n) = E_0 + (1/2)\,\bar{U} n_d(n_d-1) + (\epsilon_d^{\rm LDA} + \Delta\epsilon_d) n_d$. Note, that part of $\Delta\epsilon_d$ just arises to cancel the Coulomb contribution $(1/2)\, d[\bar{U} n_d(n_d-1)]/dn_d = \bar{U}(n_d - 1/2)$. We can, therefore, determine $\bar{U}$ and $\Delta\epsilon_d$ by fitting these parameters to reproduce the constrained LDA energies. That is, we require that Hamiltonian (13) correctly reproduces the LDA energy for three different numbers of interacting electrons on the decoupled site. Similarly, the Hund's exchange J can be calculated by constrained LDA calculations with the spin polarization. One should keep in mind that, while the total LDA spectrum is rather insensitive to the choice of the basis, the constrained LDA calculations of U strongly depends on the shape of the orbitals which are considered to be interacting. E.g., for $\rm LaTiO_3$ at a Wigner Seitz radius of 2.37 a.u. for Ti a LMTO-ASA calculation[17] using the TB-LMTO-ASA code[12] yielded $\bar{U} = 4.2$ eV in comparison to the value $\bar{U} = 3.2$ eV calculated by ASA-LMTO within orthogonal representation.[18] Thus, an appropriate basis is mandatory and, even so, a significant uncertainty in U remains.

In the following, it is convenient to work in reciprocal space where the matrix elements of $\hat{H}^0_{\rm LDA}$, i.e., the LDA one-particle energies without the local Coulomb interaction, are given by

$$(H^0_{\rm LDA}(\mathbf{k}))_{qlm,q'l'm'} = (H_{\rm LDA}(\mathbf{k}))_{qlm,q'l'm'} - \delta_{qlm,q'l'm'}\delta_{ql,q_dl_d}\Delta\epsilon_d \hat{n}_d. \tag{15}$$

Here, q is an index of the atom in the primitive cell, $(H_{\rm LDA}(\mathbf{k}))_{qlm,q'l'm'}$ is the matrix element of (11) in k-space, and q_d denotes the atoms with interacting orbitals in the primitive cell. The non-interacting part, $\hat{H}^0_{\rm LDA}$, supplemented with the local Coulomb interaction forms the (approximated) *ab initio* Hamiltonian for a particular material under investigation:

$$\begin{aligned} \hat{H} &= \hat{H}^0_{\rm LDA} + \frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'\sigma'}{}' U^{\sigma\sigma'}_{mm'}\hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma'} \\ &\quad -\frac{1}{2}\sum_{i=i_d,l=l_d}\sum_{m\sigma,m'}{}' J_{mm'}\hat{c}^\dagger_{ilm\sigma}\hat{c}^\dagger_{ilm'\bar{\sigma}}\hat{c}_{ilm'\sigma}\hat{c}_{ilm\bar{\sigma}}. \end{aligned} \tag{16}$$

2.5 Dynamical mean-field theory

The many-body extension of LDA, Eq. (16), was proposed by Anisimov *et al.*[19] in the context of their LDA+U approach. Within LDA+U the Coulomb interactions of (16) are treated within the Hartree-Fock approximation. Hence, LDA+U does not contain true many-body physics. While this approach is successful in describing long-range ordered, insulating states of correlated electronic systems it fails to describe strongly correlated *paramagnetic* states. To go beyond LDA+U and capture the many-body nature of the electron-electron interaction, i.e., the frequency dependence of the self energy, various approximation schemes have been proposed and

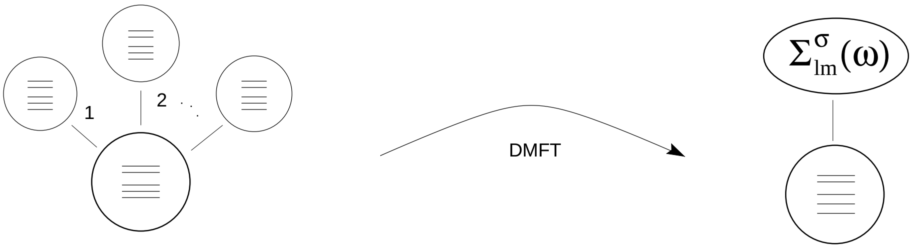


Figure 4: If the number of neighboring lattice sites goes to infinity, the central limit theorem holds and fluctuations from site-to-site can be neglected. This means that the influence of these neighboring sites can be replaced by a mean influence, the dynamical mean-field described by the self energy $\Sigma^{\sigma}_{lm}(\omega)$. This DMFT problem is equivalent to the self-consistent solution of the k-integrated Dyson equation (19) and the multi-band Anderson impurity model Eq. (18). Similar in nature are the coherent potential approximation (CPA) for disorder and the Weiss mean-field theory for spin systems. Indeed, DMFT reduces to these approximations if there is disorder and no Coulomb interaction or if the electrons can be described effectively as localized spins, respectively.

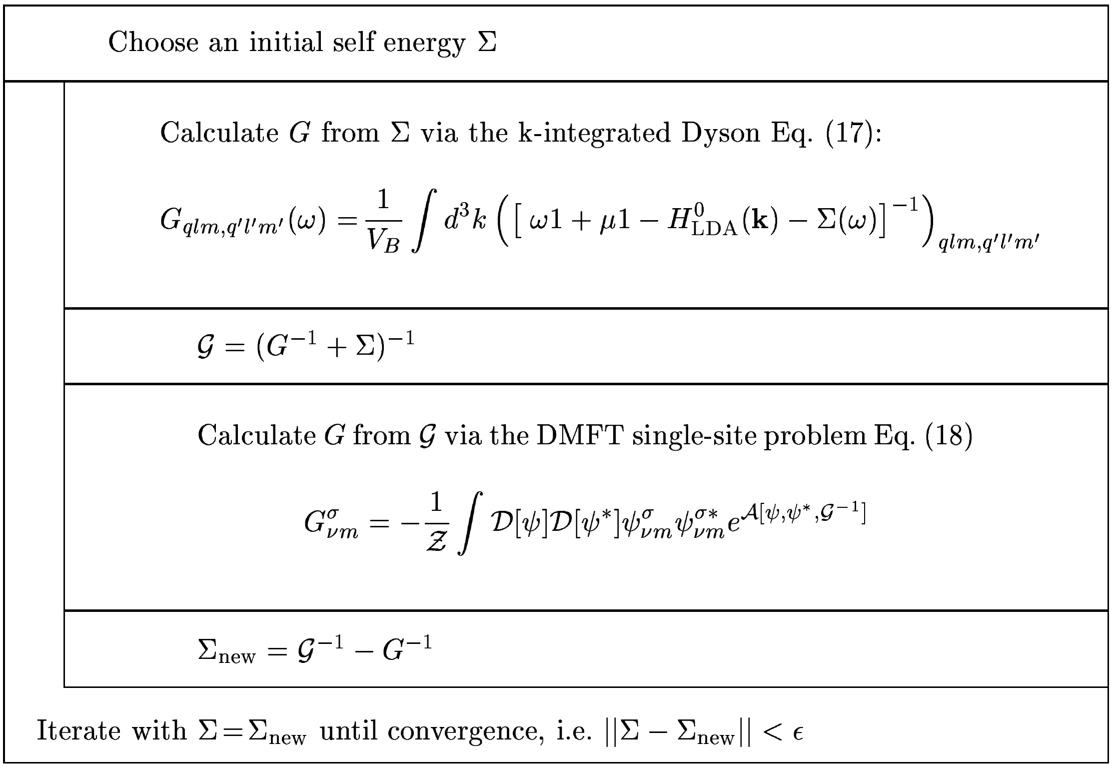
applied recently.[20–25] One of the most promising approaches, first implemented by Anisimov et al.,[20] is to solve (16) within DMFT[14, 26–33] ("LDA+DMFT"). Of all extensions of LDA only the LDA+DMFT approach is presently able to describe the physics of *strongly* correlated, paramagnetic metals with well-developed upper and lower Hubbard bands and a narrow quasiparticle peak at the Fermi level. This characteristic three-peak structure is a signature of the importance of many-body effects.[29, 30]

During the last ten years, DMFT has proved to be a successful approach for investigating strongly correlated systems with local Coulomb interactions.[33] It becomes exact in the limit of high lattice coordination numbers or dimension d, i.e., it is controlled in $1/d$,[14, 26] and preserves the dynamics of local interactions. Hence, it represents a *dynamical* mean-field approximation. In this non-perturbative approach the lattice problem is mapped onto an effective single-site problem (see Fig. 4) which has to be determined self-consistently together with the k-integrated Dyson equation connecting the self energy Σ and the on-site (or in cell) Green function G at frequency ω:

$$G_{qlm,q'l'm'}(\omega) = \frac{1}{V_B} \int d^3k \; \left(\left[\, \omega 1 + \mu 1 - H^0_{\mathrm{LDA}}(\mathbf{k}) - \Sigma(\omega) \right]^{-1} \right)_{qlm,q'l'm'} . \tag{17}$$

Here, 1 is the unit matrix, μ the chemical potential, the matrix $H^0_{\mathrm{LDA}}(\mathbf{k})$ is defined in (15), $\Sigma(\omega)$ denotes the self energy matrix which is non-zero only between the interacting orbitals, $[...]^{-1}$ implies the inversion of the matrix with elements n $(=qlm)$, $n'(=q'l'm')$, and the integration extends over the Brillouin zone with volume V_B.

The DMFT single-site problem depends on (the Weiss field) $\mathcal{G}(\omega)^{-1} = G(\omega)^{-1} + \Sigma(\omega)$ and is equivalent[29, 30] to an Anderson impurity model (the history and the physics of this model is summarized by Anderson in Ref. 34) if its hybridization $\Delta(\omega)$ satisfies $\mathcal{G}^{-1}(\omega) = \omega - \int d\omega' \Delta(\omega')/(\omega - \omega')$. The local one-particle Green function at a Matsubara frequency $i\omega_\nu = i(2\nu + 1)\pi/\beta$ (β: inverse temperature), orbital index m ($l = l_d$, $q = q_d$), and spin σ is given by the following functional integral over Grassmann variables ψ and ψ^* (for an introduction to anti-commuting



Choose an initial self energy Σ

Calculate G from Σ via the k-integrated Dyson Eq. (17):

$$G_{qlm,q'l'm'}(\omega) = \frac{1}{V_B}\int d^3k \left(\left[\,\omega 1 + \mu 1 - H^0_{\mathrm{LDA}}(\mathbf{k}) - \Sigma(\omega)\right]^{-1}\right)_{qlm,q'l'm'}$$

$$\mathcal{G} = (G^{-1} + \Sigma)^{-1}$$

Calculate G from $\mathcal{G}$ via the DMFT single-site problem Eq. (18)

$$G^{\sigma}_{\nu m} = -\frac{1}{\mathcal{Z}}\int \mathcal{D}[\psi]\mathcal{D}[\psi^*]\psi^{\sigma}_{\nu m}\psi^{\sigma *}_{\nu m} e^{\mathcal{A}[\psi,\psi^*,\mathcal{G}^{-1}]}$$

$$\Sigma_{\mathrm{new}} = \mathcal{G}^{-1} - G^{-1}$$

Iterate with $\Sigma = \Sigma_{\mathrm{new}}$ until convergence, i.e. $||\Sigma - \Sigma_{\mathrm{new}}|| < \epsilon$

Figure 5: Flow diagram of the DMFT self-consistency cycle.

Grassmann variables see Ref. 35):

$$G^{\sigma}_{\nu m} = -\frac{1}{\mathcal{Z}}\int \mathcal{D}[\psi]\mathcal{D}[\psi^*]\psi^{\sigma}_{\nu m}\psi^{\sigma *}_{\nu m} e^{\mathcal{A}[\psi,\psi^*,\mathcal{G}^{-1}]}. \tag{18}$$

Here, $\mathcal{Z} = \int \mathcal{D}[\psi]\mathcal{D}[\psi^*]\psi^{\sigma}_{\nu m}\psi^{\sigma *}_{\nu m}\exp(\mathcal{A}[\psi,\psi^*,\mathcal{G}^{-1}])$ is the partition function and the single-site action $\mathcal{A}$ has the form (the interaction part of $\mathcal{A}$ is in terms of the "imaginary time" τ, i.e., the Fourier transform of ω_ν)

$$\begin{aligned}\mathcal{A}[\psi,\psi^*,\mathcal{G}^{-1}] = &\sum_{\nu,\sigma,m} \psi^{\sigma *}_{\nu m}(\mathcal{G}^{\sigma}_{\nu m})^{-1}\psi^{\sigma}_{\nu m} \\ &-\frac{1}{2}\sum_{m\sigma,m\sigma'}{}' U^{\sigma\sigma'}_{mm'}\int_0^\beta d\tau\, \psi^{\sigma *}_{m}(\tau)\psi^{\sigma}_{m}(\tau)\psi^{\sigma' *}_{m'}(\tau)\psi^{\sigma'}_{m'}(\tau) \\ &+\frac{1}{2}\sum_{m\sigma,m}{}' J_{mm'}\int_0^\beta d\tau\, \psi^{\sigma *}_{m}(\tau)\psi^{\bar{\sigma}}_{m}(\tau)\psi^{\bar{\sigma} *}_{m'}(\tau)\psi^{\sigma}_{m'}(\tau)\ .\end{aligned} \tag{19}$$

This single-site problem (18) has to be solved self-consistently together with the **k**-integrated Dyson equation (17) to obtain the DMFT solution of a given problem, see the flow diagram Fig. 5.

Due to the equivalence of the DMFT single-site problem and the Anderson impurity problem a variety of approximate techniques have been employed to solve the DMFT equations, such as the iterated perturbation theory (IPT)[29,33] and the non-crossing approximation (NCA),[36–38] as well as numerical techniques like quantum Monte Carlo simulations (QMC),[39–42] exact diagonalization (ED),[33,43] or numerical renormalization group (NRG).[44] QMC and NCA will be discussed in more detail in Section 2.6 and 2.7, respectively. IPT is non-self-consistent second-order perturbation theory in U for the Anderson impurity problem (18) at half filling. It represents an ansatz that also yields the correct perturbational U^2-term and the correct atomic limit for the self energy off half filling,[45] for further details see Refs. 20, 21, 45. ED directly diagonalizes the Anderson impurity problem at a limited number of lattice sites and orbitals. NRG first replaces the conduction band by a discrete set of states at $D\Lambda^{-n}$ (D: bandwidth; $n = 0, ..., \mathcal{N}_s$) and then diagonalizes this problem iteratively with increasing accuracy at low energies, i.e., with increasing $\mathcal{N}_s$. In principle, QMC and ED are exact methods, but they require an extrapolation, i.e., the discretization of the imaginary time $\Delta\tau \to 0$ (QMC) or the number of lattice sites of the respective impurity model $N_s \to \infty$ (ED), respectively.

In the context of LDA+DMFT we refer to the computational schemes to solve the DMFT equations discussed above as LDA+DMFT(X) where X=IPT,[20] NCA,[25] QMC[17] have been investigated in the case of $La_{1-x}Sr_xTiO_3$. The same strategy was formulated by Lichtenstein and Katsnelson[21] as one of their LDA++ approaches. Lichtenstein and Katsnelson applied LDA+DMFT(IPT),[46] and were the first to use LDA+DMFT(QMC),[47] to investigate the spectral properties of iron. Recently, among others V_2O_3,[48,49] Ca(Sr)VO_3,[50] LiV_2O_4,[51] $Ca_{2-x}Sr_xRuO_4$,[52,53] CrO_2,[54] Ni,[55] Fe,[55] Mn,[56] Pu,[57,58] and Ce[59–61] have been studied by LDA+DMFT. Realistic investigations of itinerant ferromagnets (e.g., Ni) have also recently become possible by combining density functional theory with multi-band Gutzwiller wave functions.[62]

2.6 QMC method to solve DMFT

The self-consistency cycle of the DMFT (Fig. 5) requires a method to solve for the dynamics of the single-site problem of DMFT, i.e., Eq. (18). The QMC algorithm by Hirsch and Fye[39] is a well established method to find a numerically exact solution for the Anderson impurity model and allows one to calculate the impurity Green function G at a given $\mathcal{G}^{-1}$ as well as correlation functions. In essence, the QMC technique maps the interacting electron problem Eq. (18) onto a sum of non-interacting problems where the single particle moves in a fluctuating, time-dependent field and evaluates this sum by Monte Carlo sampling, see the flow diagram Fig. 6 for an overview. To this end, the imaginary time interval $[0, \beta]$ of the functional integral Eq. (18) is discretized into Λ steps of size $\Delta\tau = \beta/\Lambda$, yielding support points $\tau_l = l\Delta\tau$ with $l = 1 \dots \Lambda$. Using this Trotter discretization, the integral $\int_0^\beta d\tau$ is transformed to the sum $\sum_{l=1}^{\Lambda} \Delta\tau$ and the exponential terms in Eq. (18) can be separated via the Trotter-Suzuki formula for operators $\hat{A}$ and $\hat{B}$[63]

$$e^{-\beta(\hat{A}+\hat{B})} = \prod_{l=1}^{\Lambda} e^{-\Delta\tau\hat{A}} e^{-\Delta\tau\hat{B}} + \mathcal{O}(\Delta\tau), \tag{20}$$

which is exact in the limit $\Delta\tau \to 0$. The single site action $\mathcal{A}$ of Eq. (19) can now be written in the discrete, imaginary time as

$$\mathcal{A}[\psi, \psi^*, \mathcal{G}^{-1}] \;=\; \Delta\tau^2 \sum_{\sigma\, m\, l,l'=0}^{\Lambda-1} \psi^{\sigma}_{ml}{}^{*} \mathcal{G}^{\sigma}_{m}{}^{-1}(l\Delta\tau - l'\Delta\tau)\psi^{\sigma}_{ml'}$$

$$-\frac{1}{2}\Delta\tau{\sum}'_{m\sigma,m'\sigma'}U^{\sigma\sigma'}_{mm'}\sum_{l=0}^{\Lambda-1}{\psi^{\sigma}_{ml}}^{*}\psi^{\sigma}_{ml}{\psi^{\sigma'}_{m'l}}^{*}\psi^{\sigma'}_{m'l}, \tag{21}$$

where the first term was Fourier-transformed from Matsubara frequencies to imaginary time. In a second step, the $M(2M-1)$ interaction terms in the single site action $\mathcal{A}$ are decoupled by introducing a classical auxiliary field $s^{\sigma\sigma'}_{lmm'}$:

$$\begin{aligned}&\exp\left\{\frac{\Delta\tau}{2}U^{\sigma\sigma'}_{mm'}({\psi^{\sigma}_{ml}}^{*}\psi^{\sigma}_{ml}-{\psi^{\sigma'}_{m'l}}^{*}\psi^{\sigma'}_{m'l})^{2}\right\}=\\ \frac{1}{2}&\sum_{s^{\sigma\sigma'}_{lmm'}=\pm1}\exp\left\{\Delta\tau\lambda^{\sigma\sigma'}_{lmm'}s^{\sigma\sigma'}_{lmm'}({\psi^{\sigma}_{ml}}^{*}\psi^{\sigma}_{ml}-{\psi^{\sigma'}_{m'l}}^{*}\psi^{\sigma'}_{m'l})\right\},\end{aligned} \tag{22}$$

where $\cosh(\lambda^{\sigma\sigma'}_{lmm'})=\exp(\Delta\tau U^{\sigma\sigma'}_{mm'}/2)$ and M is the number of interacting orbitals. This so-called discrete Hirsch-Fye-Hubbard-Stratonovich transformation can be applied to the Coulomb repulsion as well as the Z-component of Hund's rule coupling.[64] It replaces the interacting system by a sum of $\Lambda M(2M-1)$ auxiliary fields $s^{\sigma\sigma'}_{lmm'}$. The functional integral can now be solved by a simple Gauss integration because the Fermion operators only enter quadratically, i.e., for a given configuration $\mathbf{s}=\{s^{\sigma\sigma'}_{lmm'}\}$ of the auxiliary fields the system is non-interacting. The quantum mechanical problem is then reduced to a matrix problem

$$G^{\tilde{\sigma}}_{\tilde{m}l_1l_2}=\frac{1}{\mathcal{Z}}\frac{1}{2}\sum_{l}\sum_{m'\sigma',m''\sigma''}{}'\sum_{s^{\sigma''\sigma'}_{lm''m'}=\pm1}\left[(M^{\tilde{\sigma}\mathbf{s}}_{\tilde{m}})^{-1}\right]_{l_1l_2}\prod_{m\sigma}\det\mathbf{M}^{\sigma\mathbf{s}}_{m} \tag{23}$$

with the partition function $\mathcal{Z}$, the matrix

$$\mathbf{M}^{\tilde{\sigma}\mathbf{s}}_{\tilde{m}}=\Delta\tau^{2}[{\mathbf{G}^{\sigma}_{m}}^{-1}+\Sigma^{\sigma}_{m}]e^{-\tilde{\lambda}^{\sigma\mathbf{s}}_{m}}+\mathbf{1}-e^{-\tilde{\lambda}^{\sigma\mathbf{s}}_{m}} \tag{24}$$

and the elements of the matrix $\tilde{\lambda}^{\sigma\mathbf{s}}_{m}$

$$\tilde{\lambda}^{\sigma\mathbf{s}}_{mll'}=-\delta_{ll'}\sum_{m'\sigma'}\lambda^{\sigma\sigma'}_{mm'}\tilde{\sigma}^{\sigma\sigma'}_{mm'}s^{\sigma\sigma'}_{lmm'}. \tag{25}$$

Here $\tilde{\sigma}^{\sigma\sigma'}_{mm'}=2\Theta(\sigma'-\sigma+\delta_{\sigma\sigma'}[m'-m]-1)$ changes sign if $(m\sigma)$ and $(m'\sigma')$ are exchanged. For more details, e.g., for a derivation of Eq. (24) for the matrix $\mathbf{M}$, see Refs. 33, 39.

Since the sum in Eq. (23) consists of $2^{\Lambda M(2M-1)}$ addends, a complete summation for large Λ is computationally impossible. Therefore the Monte Carlo method, which is often an efficient way to calculate high-dimensional sums and integrals, is employed for importance sampling of Eq. (23). In this method, the integrand $F(x)$ is split up into a normalized probability distribution P and the remaining term O:

$$\int dxF(x)=\int dx\,O(x)\,P(x)\equiv\langle O\rangle_{P} \tag{26}$$

with

$$\int dxP(x)=1\qquad\text{and}\qquad P(x)\geq0. \tag{27}$$

In statistical physics, the Boltzmann distribution is often a good choice for the function P:

$$P(x)=\frac{1}{\mathcal{Z}}\exp(-\beta E(x)). \tag{28}$$

```
Choose random auxiliary field configuration $\mathbf{s} = \{s^{\sigma\sigma'}_{lmm'}\}$
Calculate the current Green function $\mathbf{G}_{\text{cur}}$ from Eq. (30)
    $(G_{\text{cur}})^{\tilde{\sigma}}_{\tilde{m}l_1l_2} = \left[(M^{\tilde{\sigma}\mathbf{s}}_{\tilde{m}})^{-1}\right]_{l_1l_2}$
with $\mathbf{M}$ from Eq. (24) and the input $\mathcal{G}^{\sigma}_{m}(\omega_\nu)^{-1} = G^{\sigma}_{m}(\omega_\nu)^{-1} + \Sigma^{\sigma}_{m}(\omega_\nu)$.
Do NWU times (warm up sweeps)
    MC-sweep $(\mathbf{G}_{\text{cur}}, \mathbf{s})$
Do NMC times (measurement sweeps)
    MC-sweep $(\mathbf{G}_{\text{cur}}, \mathbf{s})$
    $\mathbf{G} = \mathbf{G} + \mathbf{G}_{\text{cur}}/\text{NMC}$
```

Figure 6: Flow diagram of the QMC algorithm to calculate the Green function matrix **G** using the procedure *MC-sweep* of Fig. 7.

For the sum of Eq. (23), this probability distribution translates to

$$P(\mathbf{s}) = \frac{1}{\mathcal{Z}} \prod_{m\sigma} \det \mathbf{M}^{\sigma\mathbf{s}}_{m} \tag{29}$$

with the remaining term

$$O(\mathbf{s})^{\tilde{\sigma}}_{\tilde{m}l_1l_2} = \left[(M^{\tilde{\sigma}\mathbf{s}}_{\tilde{m}})^{-1}\right]_{l_1l_2}. \tag{30}$$

Instead of summing over all possible configurations, the Monte Carlo simulation generates configurations x_i according to the probability distribution $P(x)$ and averages the observable $O(x)$ over these x_i. Therefore the relevant parts of the phase space with a large Boltzmann weight are taken into account to a greater extent than the ones with a small weight, coining the name importance sampling for this method. With the central limit theorem one gets for $\mathcal{N}$ statistically independent addends the estimate

$$\langle O \rangle_P = \frac{1}{\mathcal{N}} \sum_{x_i \in P(x) i=1}^{\mathcal{N}} O(x_i) \pm \frac{1}{\sqrt{\mathcal{N}}} \sqrt{\langle O^2 \rangle_P - \langle O \rangle_P^2}. \tag{31}$$

Here, the error and with it the number of needed addends $\mathcal{N}$ is nearly independent of the dimension of the integral. The computational effort for the Monte Carlo method is therefore only rising polynomially with the dimension of the integral and not exponentially as in a normal integration. Using a Markov process and single spin-flips in the auxiliary fields, the computational cost of the algorithm in leading order of Λ is

$$2aM(2M-1)\Lambda^3 \times \text{number of MC-sweeps}, \tag{32}$$

where a is the acceptance rate for a single spin-flip.

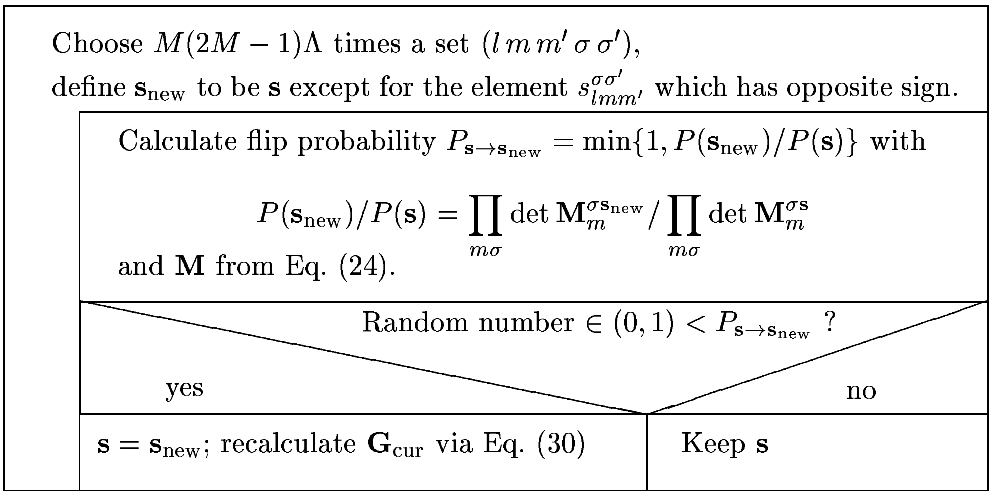


Figure 7: Procedure *MC-sweep* using the Metropolis[65] rule to change the sign of $s^{\sigma\sigma'}_{lmm'}$. The recalculation of $\mathbf{G}_{\text{cur}}$, i.e., the matrix $\mathbf{M}$ of Eq. (24), simplifies to $\mathcal{O}(\Lambda^2)$ operations if only one $s^{\sigma\sigma'}_{lmm'}$ changes sign.[33,39]

The advantage of the QMC method (for the algorithm see the flow diagram Fig. 6) is that it is (numerically) exact. It allows one to calculate the one-particle Green function as well as two-particle (or higher) Green functions. On present workstations the QMC approach is able to deal with up to seven *interacting* orbitals and temperatures above about room temperature. Very low temperatures are not accessible because the numerical effort grows like $\Lambda^3 \propto 1/T^3$. Since the QMC approach calculates $G(\tau)$ or $G(i\omega_n)$ with a statistical error, it also requires the maximum entropy method[66] to obtain the Green function $G(\omega)$ at real (physical) frequencies ω.

2.7 NCA method to solve DMFT

The NCA approach is a resolvent perturbation theory in the hybridization parameter $\Delta(\omega)$ of the effective Anderson impurity problem.[36] Thus, it is reliable if the Coulomb interaction U is large compared to the band-width and also offers a computationally inexpensive approach to check the general spectral features in other situations.

To see how the NCA can be adapted for the DMFT, let us rewrite Eq. (17) as

$$G_\sigma(z) = \frac{1}{N_k}\sum_{\mathbf{k}} [z - H^0_{LDA}(\mathbf{k}) - \Sigma_\sigma(z)]^{-1} \tag{33}$$

where $z = \omega + i0^+ + \mu$. Again, $H^0_{LDA}(\mathbf{k})$, $\Sigma_\sigma(z)$ and, hence, $G^0_\sigma(\zeta)$ and $G_\sigma(z)$ are matrices in orbital space. Note that $\Sigma(z)$ has nonzero entries for the correlated orbitals only.

On quite general grounds, Eq. (33) can be cast into the form

$$G_\sigma(z) = \frac{1}{z - E^0 - \Sigma_\sigma(z) - \Delta_\sigma(z)} \tag{34}$$

where

$$E^0 = \frac{1}{N_k}\sum_{\mathbf{k}} H^0_{LDA}(\mathbf{k}) \tag{35}$$

with the number of k points N_k and

$$\lim_{\omega \to \pm\infty} \Re e\{\Delta_\sigma(\omega + i\delta)\} = 0 \ . \tag{36}$$

Given the matrix E^0, the Coulomb matrix U and the hybridization matrix $\Delta_\sigma(z)$, we are now in a position to set up a resolvent perturbation theory with respect to $\Delta_\sigma(z)$. To this end, we first have to diagonalize the local Hamiltonian

$$\begin{aligned} H_{\text{local}} = & \sum_\sigma \sum_{qml} \sum_{q'm'l'} c^\dagger_{qlm\sigma} E^0_{qlm,q'l'm'} c_{qlm\sigma} + \frac{1}{2} \sum_{m\sigma} \sum_{m'\sigma'} U^{\sigma\sigma'}_{mm'} n_{q_d l_d m\sigma} n_{q_d l_d m'\sigma'} \\ & - \frac{1}{2} \sum_{m\sigma} \sum_{m'} J_{mm'} c^\dagger_{q_d l_d m\sigma} c^\dagger_{q_d l_d m'\bar{\sigma}} c_{q_d l_d m'\sigma} c_{q_d l_d m\bar{\sigma}} \\ = & \sum_\alpha E_\alpha |\alpha\rangle\langle\alpha| \end{aligned} \tag{37}$$

with local eigenstates $|\alpha\rangle$ and energies E_α. In contrast to the QMC, this approach allows one to take into account the full Coulomb matrix plus spin-orbit coupling.

With the states $|\alpha\rangle$ defined above, the fermionic operators with quantum numbers $\kappa = (q, l, m)$ are expressed as

$$\begin{aligned} c^\dagger_{\kappa\sigma} & = \sum_{\alpha,\beta} \left(D^{\kappa\sigma}_{\beta\alpha}\right)^* |\alpha\rangle\langle\beta| \ , \\ c_{\kappa\sigma} & = \sum_{\alpha,\beta} D^{\kappa\sigma}_{\alpha\beta} |\alpha\rangle\langle\beta| \ . \end{aligned} \tag{38}$$

The key quantity for the resolvent perturbation theory is the resolvent $R(z)$, which obeys a Dyson equation[36]

$$R(z) = R^0(z) + R^0(z) S(z) R(z) \ , \tag{39}$$

where $R^0_{\alpha\beta}(z) = 1/(z - E_\alpha)\delta_{\alpha\beta}$ and $S_{\alpha\beta}(z)$ denotes the self energy for the local states due to the coupling to the environment through $\Delta(z)$.

The self energy $S_{\alpha\beta}(z)$ can be expressed as power series in the hybridization $\Delta(z)$.[36] Retaining only the lowest-, i.e. 2^{nd}-order terms leads to a set of self-consistent integral equations

$$\begin{aligned} S_{\alpha\beta}(z) = & \sum_\sigma \sum_{\kappa\kappa'} \sum_{\alpha'\beta'} \int \frac{d\varepsilon}{\pi} f(\varepsilon) \ (D^{\kappa\sigma}_{\alpha'\alpha})^* \, \Gamma^{\kappa\kappa'}_\sigma(\varepsilon) R_{\alpha'\beta'}(z + \varepsilon) D^{\kappa'\sigma}_{\beta'\beta} \\ & + \sum_\sigma \sum_{\kappa\kappa'} \sum_{\alpha'\beta'} \int \frac{d\varepsilon}{\pi} (1 - f(\varepsilon)) \, D^{\kappa\sigma}_{\alpha'\alpha} \Gamma^{\kappa\kappa'}_\sigma(\varepsilon) R_{\alpha'\beta'}(z - \varepsilon) \left(D^{\kappa'\sigma}_{\beta'\beta}\right)^* \end{aligned} \tag{40}$$

to determine $S_{\alpha\beta}(z)$, where $f(\varepsilon)$ denotes Fermi's function and $\Gamma(\varepsilon) = -\Im m \{\Delta(\varepsilon + i0^+)\}$. The set of equations (40) is in the literature referred to as non-crossing approximation (NCA), because, when viewed in terms of diagrams, these diagrams contain no crossing of band-electron lines. In order to close the cycle for the DMFT, we still have to calculate the true local Green function $G_\sigma(z)$. This, however, can be done within the same approximation with the result

$$G^{\kappa\kappa'}_\sigma(i\omega) = \frac{1}{Z_{\text{local}}} \sum_{\alpha,\alpha'} \sum_{\nu,\nu'} D^{\kappa\sigma}_{\alpha\alpha'} \left(D^{\kappa'\sigma}_{\nu\nu'}\right)^* \oint \frac{dz e^{-\beta z}}{2\pi i} R_{\alpha\nu}(z) R_{\alpha'\nu'}(z + i\omega) \ . \tag{41}$$

Here, $Z_{\text{local}} = \sum_{\alpha} \oint \frac{dze^{-\beta z}}{2\pi i} R_{\alpha\alpha}(z)$ denotes the local partition function and β is the inverse temperature.

Like any other technique, the NCA has its merits and disadvantages. As a self-consistent resummation of diagrams it constitutes a conserving approximation to the Anderson impurity model. Furthermore, it is a (computationally) fast method to obtain dynamical results for this model and thus also within DMFT. However, the NCA is known to violate Fermi liquid properties at temperatures much lower than the smallest energy scale of the problem and whenever charge excitations become dominant.[38, 67] Hence, in some parameter ranges it fails in the most dramatic way and must therefore be applied with considerable care.[38]

2.8 Simplifications for transition metal oxides with well separated e_g- and t_{2g}-bands

Many transition metal oxides are cubic perovskites, with only a slight distortion of the cubic crystal structure. In these systems the transition metal d-orbitals lead to strong Coulomb interactions between the electrons. The cubic crystal-field of the oxygen causes the d-orbitals to split into three degenerate t_{2g}- and two degenerate e_g-orbitals. This splitting is often so strong that the t_{2g}- or e_g-bands at the Fermi energy are rather well separated from all other bands. In this situation the low-energy physics is well described by taking only the degenerate bands at the Fermi energy into account. Without symmetry breaking, the Green function and the self energy of these bands remain degenerate, i.e., $G_{qlm,q'l'm'}(z) = G(z)\delta_{qlm,q'l'm'}$ and $\Sigma_{qlm,q'l'm'}(z) = \Sigma(z)\delta_{qlm,q'l'm'}$ for $l = l_d$ and $q = q_d$ (where l_d and q_d denote the electrons in the interacting band at the Fermi energy). Downfolding to a basis with these degenerate q_d-l_d-bands results in an effective Hamiltonian $H^{0\,\text{eff}}_{\text{LDA}}$ (where indices $l = l_d$ and $q = q_d$ are suppressed)

$$G_{mm'}(\omega) \;=\; \frac{1}{V_B}\int \mathrm{d}^3k \, \left([\omega 1 + \mu 1 - H^{0\,\text{eff}}_{\text{LDA}}(\mathbf{k}) - \Sigma(\omega)]^{-1}\right)_{mm'} . \tag{42}$$

Due to the diagonal structure of the self energy the degenerate interacting Green function can be expressed via the non-interacting Green function $G^0(\omega)$:

$$G(\omega) \;=\; G^0(\omega - \Sigma(\omega)) = \int d\epsilon \frac{N^0(\epsilon)}{\omega - \Sigma(\omega) - \epsilon}. \tag{43}$$

Thus, it is possible to use the Hilbert transformation of the unperturbed LDA-calculated density of states (DOS) $N^0(\epsilon)$, i.e., Eq. (43), instead of Eq. (17). This simplifies the calculations considerably. With Eq. (43) also some conceptual simplifications arise: (i) the subtraction of $\sum_{i=i_d,l=l_d} \sum_{m\sigma} \Delta\epsilon_d \, \hat{n}_{ilm\sigma}$ [see Eq. (13)] only results in an (unimportant) shift of the chemical potential in (43) and, thus, the exact form of $\Delta\epsilon_d$ is irrelevant; (ii) Luttinger's theorem of Fermi pinning holds, i.e., the interacting DOS at the Fermi energy is fixed at the value of the non-interacting DOS at $T = 0$ within a Fermi liquid; (iii) as the number of electrons within the different bands is fixed, the LDA+DMFT approach is automatically self-consistent.

3 Extensions and modifications of LDA+DMFT

3.1 Self-consistent LDA+DMFT calculations

In the present form of the LDA+DMFT scheme the band-structure input due to LDA and the inclusion of the electronic correlations by DMFT are performed as successive steps without subsequent feedback. In general, the DMFT solution will result in a change of the occupation of the different bands involved. This changes the electron density $\rho(\mathbf{r})$ and, thus, results in a new LDA-Hamiltonian $\hat{H}_{\text{LDA}}$ (11) since $\hat{H}_{\text{LDA}}$ depends on $\rho(\mathbf{r})$. At the same time also the Coulomb interaction U changes and needs to be determined by a new constrained LDA calculation. In a *self-consistent* LDA+DMFT scheme, H_{LDA} and U would define a new Hamiltonian (16) which again needs to be solved within DMFT, etc., until convergence is reached:

$$\begin{tikzcd}
\rho(\mathbf{r}) \arrow[r] & H_{\text{LDA}},\, U \arrow[r, "\text{DMFT}"] & n_{ilm} \arrow[r] & \rho(\mathbf{r}) \arrow[ll, bend left]
\end{tikzcd} \tag{44}$$

Without Coulomb interaction ($U = 0$) this scheme reduces to the self-consistent solution of the Kohn-Sham equations. A self-consistency scheme similar to Eq. (44) was employed by Savrasov and Kotliar[58] in their calculation of Pu (without self-consistency for U). The quantitative difference between non-self-consistent and self-consistent LDA+DMFT depends on the change of the number of electrons in the different bands after the DMFT calculation, which of course depends on the problem at hand. E.g., for the Ce calculation presented in Section 6, this change was very minor in the vicinity of α-γ transition but more significant at lower volumes.

In this context, we would also like to note that an *ab initio* DMFT scheme formulated directly in the continuum was recently proposed by Chitra and Kotliar.[68]

3.2 LDA+DMFT as a spectral density functional theory

Our derivation of the LDA+DMFT method was physically motivated. That is, we started from the assumption that the Kohn-Sham equations, i.e., the LDA part, yield the correct results for the weakly correlated s- or p-bands, while the DMFT-part takes into account the local Coulomb interactions of the strongly correlated d- or f-bands. Using the effective action construction by Fukuda *et al.*,[69] Savrasov *et al.*[7,57,58] embedded LDA+DMFT in a functional theory with a functional $E[G_{il_dm}(\omega), \rho(r)]$ which depends on the electron density $\rho(r)$ *and* the local Green function $G_{il_dm}(\omega)$ (thus coining the name *spectral density functional theory*[7]). This is in the spirit of density functional theory with the LDA+DMFT equations emerging from the minimization of $E[G_{il_dm}(\omega), \rho(r)]$ w.r.t. $G_{il_dm}(\omega)$ and $\rho(r)$. If the functional $E[G_{il_dm}(\omega), \rho(r)]$ were known exactly one would obtain the exact ground state energy. However, since the exact functional is unknown one has to introduce approximations. Then, LDA+DMFT is a workable approximation to the spectral density function theory, similar to LDA within DFT.

3.3 Cluster extensions of DMFT

DMFT reliably describes local correlations in terms of the local (or, equivalently k-independent) self energy $\Sigma_{il_dm,il_dm'}(\omega)$. For some problems like, e.g., fluctuations in the vicinity of a phase transition or the formation of a spin-singlet on two neighboring sites, non-local correlations are important. The standard DMFT described in Section 2.5 neglects such non-local correlations because only a single site with local correlations in an average environment (a dynamical mean-field) is considered. However, in principle, DMFT can also treat more than one site, i.e., a cell of sites, in an average environment. E.g., if the primitive contains several sites with interacting d- or f-orbitals a natural choice for the DMFT cell would be this cell. Then, non-local correlations $\Sigma_{il_dm,jl_dm'}(\omega)$ would be taken into account if i and j are within the cell, whereas such correlations would be neglected if i and j are located in different cells. Furthermore, even if the primitive contains only one interacting site one may consider a larger DMFT cell with several interacting sites, treating non-local correlations within that cell but not between different cells. This is the basic idea of cluster DMFT approaches.[33, 70–72]

An alternative scheme, named dynamical cluster approximation (DCA), has been proposed by Hettler *et al.*[73] The DCA has the advantage of preserving the translational symmetry. While cluster DMFT can be best understood in real space, it is instructive to go to k-space for DCA. Within DCA the first Brillouin zone is divided into N_c patches around k-vectors K, assuming the self energy to be constant within each patch only (in contrast to DMFT, where the self energy is constant for all k-vectors). In real space, the DCA cluster has periodic boundary conditions instead of open boundary conditions for the cluster DMFT scheme. In addition, the dynamical mean-field couples to every site of the cluster, whereas within cluster DMFT it couples exclusively to the boundary sites. Whether cluster DMFT or DCA provides a better scaling w.r.t. cluster size $N_c \to \infty$ is still a matter of debate and likely depends on the problem at hand (both approaches give the correct behavior of any finite-dimensional problem for $N_c \to \infty$). It is important to note, and not a matter of course, that all these approaches[70–73] lead to physically correct (causal) Green functions.

A third route was proposed by Schiller *et al.*[74] It is a natural extension of DMFT in the sense that it takes into account all diagrams to next order in $1/d$ (d: spatial dimension), i.e., up to order $1/d$. This leads to a theory with a single-site and a two-site cluster whose Green functions have to be subtracted.

Cluster extensions of DMFT have been applied successfully to a couple of model systems. For example, d-wave superconductivity in the two-dimensional Hubbard model mediated by spin-fluctuations was found.[71, 75] In the context of LDA+DMFT cluster extensions of DMFT are still work in progress.

3.4 GW+DMFT

A possible alternative to LDA+DMFT is the GW+DMFT[77] approach, which uses Hedin's GW approximation[76] instead of the LDA to generate the multi-band many-body problem Eq. (16) in Section 2.4. From a pure, theoretical point of view, GW+DMFT has the advantage of being a fully diagrammatic approach. This allows a better understanding of what one is actually calculating and is particularly appealing to the many-body community. One might consider GW+DMFT as the minimum set of diagrams which are necessary to realistically describe correlated materials: It contains the Hartree and exchange diagrams together with the RPA-like screening of the Coulomb interaction and, via DMFT, the important local diagrams leading to the Kondo-like and Mott-insulating physics of correlated systems. However, whether these theoretical principles can be maintained in actual calculations still needs to be seen. Problems already arise in mere GW calculations of weakly correlated systems where Coulomb interactions are (often) calculated from the (non-diagrammatic) LDA wave function instead of the self-consistent GW wave functions. GW+DMFT calculations for real materials are still work in progress.[77]

4 Comparison of different methods to solve DMFT: the model system $La_{1-x}Sr_xTiO_3$

The stoichiometric compound $LaTiO_3$ is a cubic perovskite with a small orthorhombic distortion ($\angle\, Ti-O-Ti \approx 155°$)[78] and is an antiferromagnetic insulator[79] below $T_N = 125$ K.[80] Above T_N, or at low Sr-doping x, and neglecting the small orthorhombic distortion (i.e., considering a cubic structure with the same volume), $LaTiO_3$ is a strongly correlated, but otherwise simple paramagnet with only *one* $3d$-electron on the trivalent Ti sites. This makes the system a perfect trial candidate for the LDA+DMFT approach.

The LDA band-structure calculation for undoped (cubic) $LaTiO_3$ yields the DOS shown in Fig. 8 which is typical for early transition metal oxides. The oxygen bands, ranging from -8.2 eV to -4.0 eV, are filled such that Ti has a d^1 configuration. Due to the crystal- or ligand-field splitting, the Ti $3d$-bands separate into two empty e_g-bands and three degenerate t_{2g}-bands. Since the t_{2g}-bands at the Fermi energy are well separated also from the other bands we employ the approximation introduced in section 2.5 which allows us to work with the LDA DOS [Eq. (43)] instead of the full one-particle Hamiltonian $H^0_{\rm LDA}$ of [Eq. (17)]. In the LDA+DMFT calculation, Sr-doping x is taken into account by adjusting the chemical potential to yield $n = 1 - x = 0.94$ electrons within the t_{2g}-bands, neglecting effects of disorder and the x-dependence of the LDA DOS (note, that $LaTiO_3$ and $SrTiO_3$ have a very similar band structure within LDA). There is some uncertainty in the LDA-calculated Coulomb interaction parameter $U \sim 4 - 5$ eV (for a discussion see Ref. 17) which is here assumed to be spin- and orbital-independent. In Fig. 9, results for the spectrum of $La_{0.94}Sr_{0.06}TiO_3$ as calculated by LDA+DMFT(IPT, NCA, QMC) for the same LDA DOS at $T \approx 1000$ K and $U = 4$ eV are compared.[17] In Ref. 17 the formerly presented IPT[20] and NCA[25] spectra were recalculated to allow for a comparison at exactly the same parameters. All three methods yield the typical features of strongly correlated metallic paramagnets: a lower Hubbard band, a quasi-particle peak (note that IPT produces a quasi-particle peak only below about 250K which is therefore not seen here), and an upper Hubbard band. By contrast, within LDA the correlation-induced Hubbard bands are missing and only a broad central quasi-particle band (actually a one-particle peak) is obtained (Fig. 8).

While the results of the three evaluation techniques of the DMFT equations (the approximations IPT, NCA and the numerically exact method QMC) agree on a qualitative level, Fig. 9 reveals

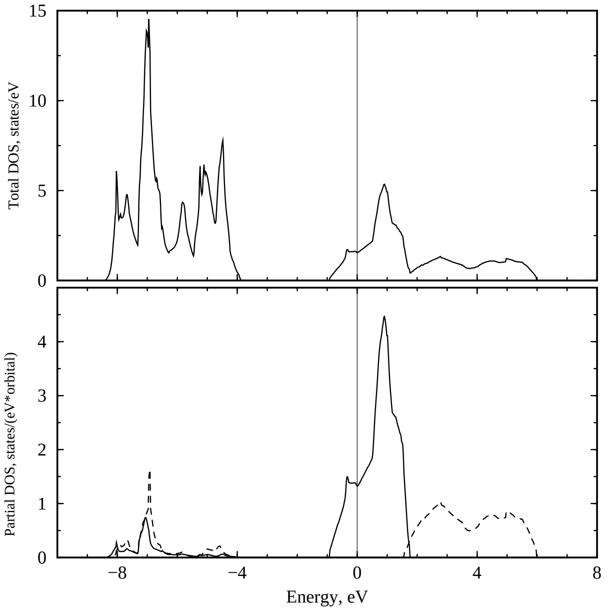


Figure 8: Densities of states of $LaTiO_3$ calculated with LDA-LMTO. Upper figure: total DOS; lower figure: partial t_{2g} (solid lines) and e_g (dashed lines) DOS [reproduced from Ref. 17].

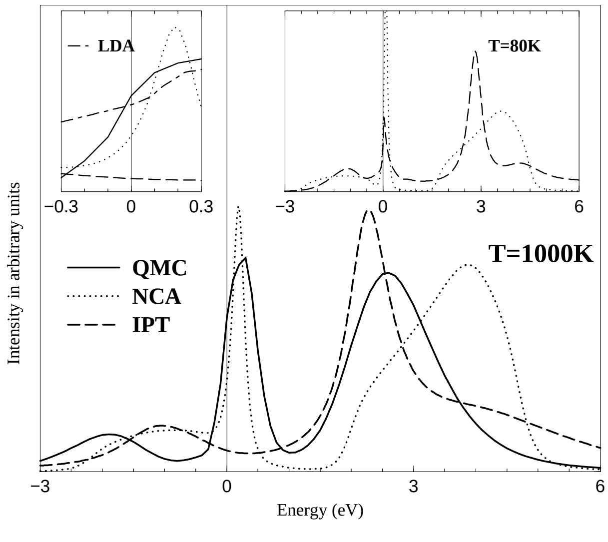


Figure 9: Spectrum of $La_{0.94}Sr_{0.06}TiO_3$ as calculated by LDA+DMFT(X) at $T = 0.1$ eV ($\approx$ 1000 K) and $U = 4$ eV employing the approximations X=IPT, NCA, and numerically exact QMC. Inset left: Behavior at the Fermi level including the LDA DOS. Inset right: X=IPT and NCA spectra at $T = 80$ K [reproduced from Ref. 17].

considerable quantitative differences. In particular, the IPT quasi-particle peak found at low temperatures (see right inset of Fig. 9) is too narrow such that it disappears already at about 250 K and is, thus, not present at $T \approx 1000$ K. A similarly narrow IPT quasi-particle peak was found in a three-band model study with Bethe-DOS by Kajueter and Kotliar.[45] Besides underestimating the Kondo temperature, IPT also produces notable deviations in the shape of the upper Hubbard band. Although NCA comes off much better than IPT it still underestimates the width of the quasiparticle peak by a factor of two. Furthermore, the position of the quasiparticle peak is too close to the lower Hubbard band. In the left inset of Fig. 9, the spectra at the Fermi level are shown. At the Fermi level, where at sufficiently low temperatures the interacting DOS should be pinned at the non-interacting value, the NCA yields a spectral function which is almost by a factor of two too small. The pinning of the interacting DOS mentioned above holds for the situation here where only degenerate bands are involved and the system is a Fermi liquid. It is due to the k-independence of the self-energy; nonetheless, the effective mass is renormalized: $m^*/m_0 = 1 - \partial \Re \Sigma(w)/\partial \omega|_{\omega=0}$. The shortcomings of the NCA-results, with a too small low-energy scale and too much broadened Hubbard bands for multi-band systems, are well understood and related to the neglect of exchange type diagrams.[82] Similarly, the deficiencies of the IPT-results are not entirely surprising in view of the semi-phenomenological nature of this approximation, especially for a system off half filling.

This comparison shows that the choice of the *method* used to solve the DMFT equations is indeed *important*, and that, at least for the present system, the approximations IPT and NCA differ quantitatively from the numerically exact QMC. Nevertheless, the NCA gives a rather good account of the qualitative spectral features and, because it is fast and can often be applied at comparatively low temperatures, can yield an overview of the physics.

Photoemission spectra provide a direct experimental tool to study the electronic structure and spectral properties of electronically correlated materials. A comparison of LDA+DMFT(QMC) at 1000 K[83] with the experimental photoemission spectrum[84] of $\mathrm{La}_{0.94}\mathrm{Sr}_{0.06}\mathrm{TiO}_3$ is presented in Fig 10. To take into account the uncertainty in U,[17] we present results for $U = 3.2$, 4.25 and 5 eV. All spectra are multiplied with the Fermi step function and are Gauss-broadened with a broadening parameter of 0.3 eV to simulate the experimental resolution.[84] LDA band structure calculations, the results of which are also presented in Fig. 10, clearly fail to reproduce the broad band observed in the experiment at 1-2 eV below the Fermi energy.[84] Taking the correlations between the electrons into account, this lower band is easily identified as the lower Hubbard band whose spectral weight originates from the quasi-particle band at the Fermi energy and which increases with U. The best agreement with experiment concerning the relative intensities of the Hubbard band and the quasi-particle peak and, also, the position of the Hubbard band is found for $U = 5$ eV. The value $U = 5$ eV is still compatible with the *ab initio* calculation of this parameter within LDA.[17] One should also bear in mind that photoemission experiments are sensitive to surface properties. Due to the reduced coordination number at the surface the bandwidth is likely to be smaller, and the Coulomb interaction less screened, i.e., larger. Both effects make the system more correlated and, thus, might also explain why better agreement is found for $U = 5$ eV. Besides that, also the polycrystalline nature of the sample, as well as spin and orbital[85] fluctuation not taken into account in the LDA+DMFT approach, will lead to a further reduction of the quasi-particle weight.

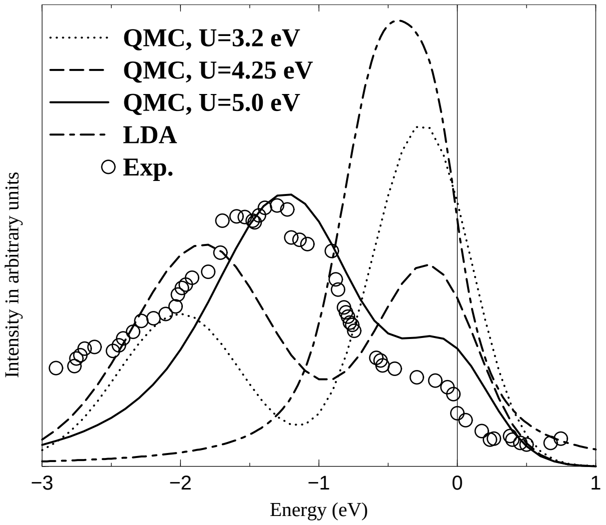


Figure 10: Comparison of the experimental photoemission spectrum,[84] the LDA result, and the LDA+DMFT(QMC) calculation for $La_{0.94}Sr_{0.06}TiO_3$ (i.e., 6% hole doping) and different Coulomb interactions $U = 3.2$, 4.25, and 5 eV [reproduced from Ref.17].

5 Mott-Hubbard metal-insulator transition in V_2O_3

One of the most famous examples of a cooperative electronic phenomenon occurring at intermediate coupling strengths is the transition between a paramagnetic metal and a paramagnetic insulator induced by the Coulomb interaction between the electrons – the Mott-Hubbard metal-insulator transition. The question concerning the nature of this transition poses one of the fundamental theoretical problems in condensed matter physics.[86] Correlation-induced metal-insulator transitions (MIT) are found, for example, in transition metal oxides with partially filled bands near the Fermi level. For such systems bandstructure theory typically predicts metallic behavior. The most famous example is V_2O_3 doped with Cr as shown in Fig. 11. While at low temperatures V_2O_3 is an antiferromagnetic insulator with monoclinic crystal symmetry, it has a corundum structure in the high-temperature paramagnetic phase. All transitions shown in the phase diagram are of first order. In the case of the transitions from the high-temperature paramagnetic phases into the low-temperature antiferromagnetic phase this is naturally explained by the fact that the transition is accompanied by a change in crystal symmetry. By contrast, the crystal symmetry across the MIT in the paramagnetic phase remains intact, since only the ratio of the c/a axes changes discontinuously. This may be taken as an indication for the predominantly electronic origin of this transition which is not accompanied by any conventional long-range order. ¿From a model point of view the MIT is triggered by a change of the ratio of the Coulomb interaction U relative to the bandwidth W. Originally, Mott considered the extreme limits $W = 0$ (when atoms are isolated and insulating) and $U = 0$ where the system is metallic. While it is simple to describe these limits, the crossover between them, i.e., the metal-insulator transition itself, poses a very complicated electronic correlation problem. Among others, this metal-insulator transition has been addressed by Hubbard in various approximations[88] and by Brinkman and Rice within the Gutzwiller approximation.[89] During the last few years, our understanding of the MIT in the one-band Hubbard model has considerably

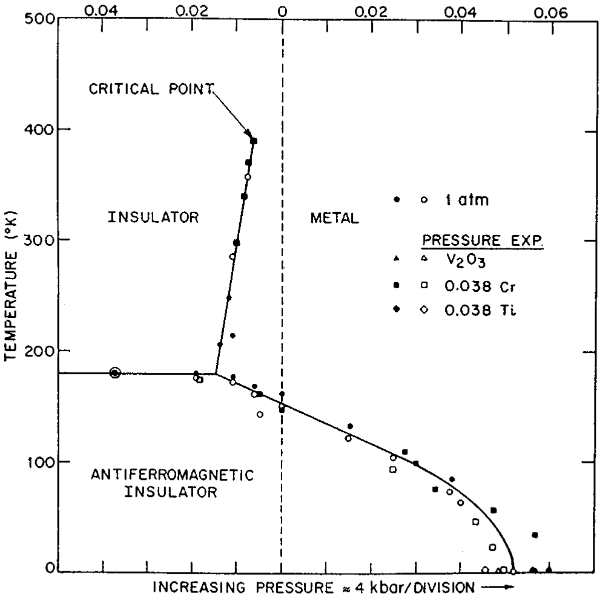


Figure 11: Experimental phase diagram of V_2O_3 doped with Cr and Ti [reproduced from Ref. 87]. Doping V_2O_3 affects the lattice constants in a similar way as applying pressure (generated either by a hydrostatic pressure P, or by changing the V-concentration from V_2O_3 to $V_{2-y}O_3$) and leads to a Mott-Hubbard transition between the *paramagnetic* insulator (PI) and metal (PM). At lower temperatures, a Mott-Heisenberg transition between the paramagnetic metal (PM) and the *antiferromagnetic* insulator (AFI) is observed.

improved, in particular due to the application of dynamical mean-field theory.[90]

Both the paramagnetic *metal* V_2O_3 and the paramagnetic *insulator* $(V_{0.962}Cr_{0.038})_2O_3$ have the same corundum crystal structure with only slightly different lattice parameters.[91,92] Nevertheless, within LDA both phases are found to be metallic (see Fig. 12). The LDA DOS shows a splitting of the five Vanadium d-orbitals into three t_{2g} states near the Fermi energy and two e_g^σ states at higher energies. This reflects the (approximate) octahedral arrangement of oxygen around the vanadium atoms. Due to the trigonal symmetry of the corundum structure the t_{2g} states are further split into one a_{1g} band and two degenerate e_g^π bands, see Fig. 12. The only visible difference between $(V_{0.962}Cr_{0.038})_2O_3$ and V_2O_3 is a slight narrowing of the t_{2g} and e_g^σ bands by ≈ 0.2 and 0.1 eV, respectively as well as a weak downshift of the centers of gravity of both groups of bands for V_2O_3. In particular, the insulating gap of the Cr-doped system is seen to be missing in the LDA DOS. Here we will employ LDA+DMFT(QMC) to show explicitly that the insulating gap is caused by electronic correlations. In particular, we make use of the simplification for transition metal oxides described in Section 2.8 and restrict the LDA+DMFT(QMC) calculation to the three t_{2g} bands at the Fermi energy, separated from the e_g^σ and oxygen bands.

While the Hund's rule coupling J is insensitive to screening effects and may, thus, be obtained within LDA to a good accuracy ($J = 0.93$ eV[18]), the LDA-calculated value of the Coulomb repulsion U has a typical uncertainty of at least 0.5 eV.[17] To overcome this uncertainty, we study the spectra obtained by LDA+DMFT(QMC) for three different values of the Hubbard interaction ($U = 4.5, 5.0, 5.5\,\mathrm{eV}$) in Fig. 13. ¿From the results obtained we conclude that the critical value of U for the MIT is at about 5 eV: At $U = 4.5$ eV one observes pronounced

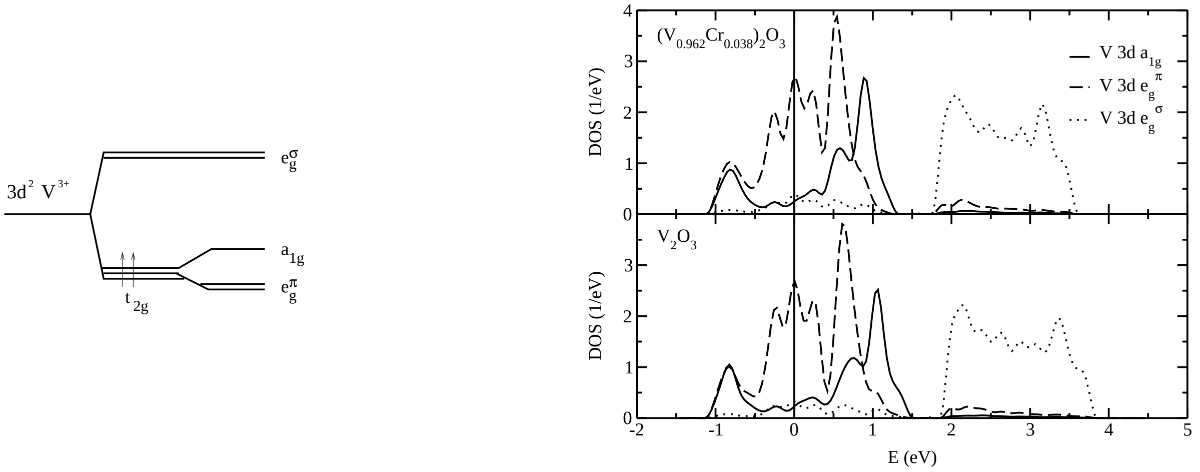


Figure 12: Left: Scheme of the $3d$ levels in the corundum crystal structure. Right: Partial LDA DOS of the 3d bands for paramagnetic metallic V_2O_3 and insulating $(V_{0.962}Cr_{0.038})_2O_3$ [reproduced from Ref. 48].

quasiparticle peaks at the Fermi energy, i.e., characteristic metallic behavior, even for the crystal structure of the insulator $(V_{0.962}Cr_{0.038})_2O_3$, while at $U = 5.5$ eV the form of the calculated spectral function is typical for an insulator for both sets of crystal structure parameters. At $U = 5.0$ eV one is then at, or very close to, the MIT since there is a pronounced dip in the DOS at the Fermi energy for both a_{1g} and e_g^π orbitals for the crystal structure of $(V_{0.962}Cr_{0.038})_2O_3$, while for pure V_2O_3 one still finds quasiparticle peaks. (We note that at $T \approx 0.1$ eV one only observes metallic-like and insulator-like behavior, with a rapid but smooth crossover between these two phases, since a sharp MIT occurs only at lower temperatures[40,90]). The critical value of the Coulomb interaction $U \approx 5$ eV is in reasonable agreement with the values determined spectroscopically by fitting to model calculations, and by constrained LDA, see Ref. 48 for details.

To compare with the V_2O_3 photoemission spectra by Schramme *et al.*[93] and Mo *et al.*,[94] as well as with the X-ray absorption data by Müller *et al.*,[95] the LDA+DMFT(QMC) spectrum at $T = 300\,\mathrm{K}$ is multiplied with the Fermi function and Gauss-broadened by 0.09 eV to account for the experimental resolution. The theoretical result for $U = 5$ eV is seen to be in good agreement with experiment (Fig. 14). In contrast to the LDA results, our results do not only describe the different bandwidths above *and* below the Fermi energy (≈ 6 eV and $\approx 2-3$ eV, respectively), but also the position of two (hardly distinguishable) peaks below the Fermi energy (at about -1 eV and -0.3 eV) as well as the pronounced two-peak structure above the Fermi energy (at about 1 eV and 3-4 eV). In our calculation the e_g^σ states have not been included so far. Taking into account the Coulomb interaction $\bar{U} = U - 2J \approx 3\,\mathrm{eV}$ and also the difference between the e_g^σ- and t_{2g}-band centers of gravity of roughly 2.5 eV, the e_g^σ-band can be expected to be located roughly 5.5 eV above the lower Hubbard band (-1.5 eV), i.e., at about 4 eV. From this estimate one would conclude the upper X-ray absorption maximum around 4 eV in Fig. 12 to be of mixed e_g^σ and e_g^π nature.

While LDA also gives two peaks below and above the Fermi energy, their position and physical origin is quite different. Within LDA+DMFT(QMC) the peaks at -1 eV and 3-4 eV are the incoherent Hubbard bands induced by the electronic correlations whereas in the LDA the peak

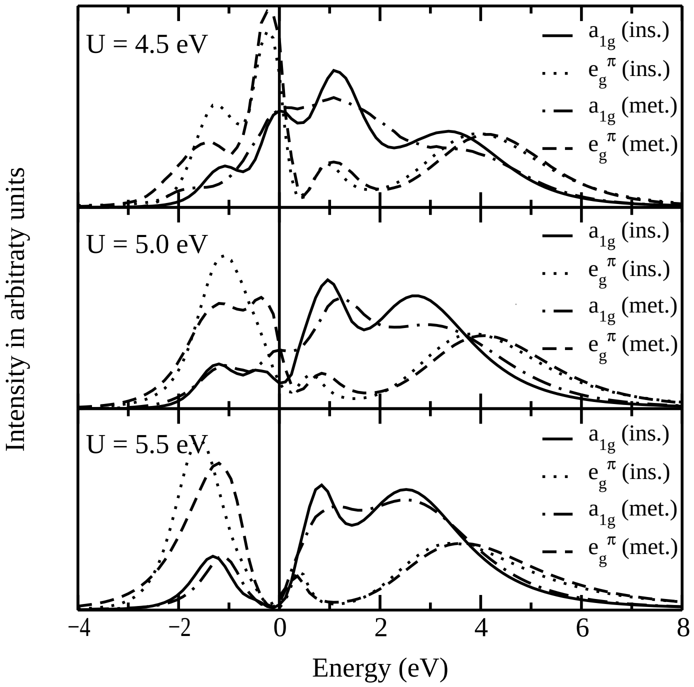


Figure 13: LDA+DMFT(QMC) spectra for paramagnetic $(V_{0.962}Cr_{0.038})_2O_3$ ("ins.") and V_2O_3 ("met.") at $U = 4.5$, 5 and 5.5 eV, and $T = 0.1$ eV = 1160 K [reproduced from Ref.48].

at 2-3 eV is caused entirely by (one-particle) e_g^σ states, and that at -1 eV is the band edge maximum of the a_{1g} and e_g^π states (see Fig. 12). Obviously, the LDA+DMFT results are a big improvement over LDA which, as one should keep in mind, was the best method available to calculate the V_2O_3 spectrum before. Still there remain some differences between theory and experiment which might, among other reasons, be due to the fact that every V ion has a unique neighbor in one direction, i.e., the LDA supercell calculation has *a pair* of V ions per primitive cell, or due to short-range antiferromagnetic correlations in the vicinity of the antiferromagnetic transition (175 K is close to the Néel temperature).

Particularly interesting are the spin and the orbital degrees of freedom in V_2O_3. From our calculations,[48] we conclude that the spin state of V_2O_3 is $S = 1$ throughout the Mott-Hubbard transition region. This agrees with the measurements of Park *et al.*[96] and also with the data for the high-temperature susceptibility.[97] But, it is at odds with the $S = 1/2$ model by Castellani *et al.*[98] and with the results[99] for a one-band Hubbard model which corresponds to $S = 1/2$ in the insulating phase and, contrary to our results, shows a substantial change of the local magnetic moment at the MIT.[90] For the orbital degrees of freedom we find a predominant occupation of the e_g^π orbitals, but with a significant admixture of a_{1g} orbitals. This admixture decreases at the MIT: in the metallic phase at $T = 0.1$ eV we determine the occupation of the $(a_{1g}, e_{g1}^\pi, e_{g2}^\pi)$ orbitals as (0.37, 0.815, 0.815), and in the insulating phase as (0.28, 0.86, 0.86). This should be compared with the experimental results of Park *et al.*[96] From their analysis of the linear dichroism data the authors concluded that the ratio of the configurations $e_g^\pi e_g^\pi$:$e_g^\pi a_{1g}$ is equal to 1:1 for the paramagnetic metallic and 3:2 for the paramagnetic insulating phase, corresponding to a one-electron occupation of (0.5,0.75,0.75) and (0.4,0.8,0.8), respectively. Although our results show a somewhat smaller value for the admixture of a_{1g} orbitals, the overall behavior,

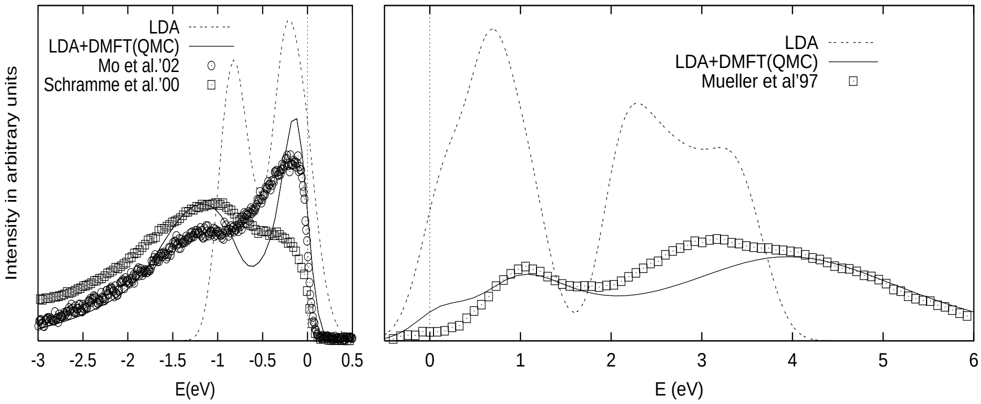


Figure 14: Comparison of the LDA+DMFT(QMC) spectrum[48] at $U = 5\,\mathrm{eV}$ and $T = 300\,\mathrm{K}$ below (left Figure) and above (right Figure) the Fermi energy (at 0 eV) with the LDA spectrum[48] and the experimental spectrum (left: photoemission spectrum of Schramme *et al.*[93] at $T = 300\,\mathrm{K}$ and Mo *et al.* at $T = 175\,\mathrm{K}$;[94] right: X-ray absorption spectrum of Müller *et al.* at $T = 300\,\mathrm{K}$[95]). Note that Mo *et al.*[94] use a higher photon energy ($h\nu = 500\,\mathrm{eV}$) than Schramme *et al.*[93] ($h\nu = 60\,\mathrm{eV}$) which considerably reduces the surface contribution to the spectrum.

including the tendency of a *decrease* of the a_{1g} admixture across the transition to the insulating state, are well reproduced. In this context we would also like to note the work by Laad *et al.*[49] who started from our LDA DOS for V_2O_3 and found, within DMFT(IPT), that it is possible to trigger a Mott-Hubbard metal-insulator transition by shifting the e_g^{π}-band with respect to the a_{1g}-band.

In the study above, the experimental crystal parameters of V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$ have been taken from the experiment. This leaves the question unanswered whether a change of the lattice is the driving force behind the Mott transition, or whether it is the electronic Mott transition which causes a change of the lattice. For another system, Ce, we will show in Section 6 that the energetic changes near a Mott transition are indeed sufficient to cause a first-order volume change.

6 The Cerium volume collapse: An example for a 4f-electron system

Cerium exhibits a transition from the γ- to the α-phase with increasing pressure or decreasing temperature. This transition is accompanied by an unusually large volume change of 15%,[100] much larger than the 1-2% volume change in V_2O_3. The γ-phase may also be prepared in metastable form at room temperature in which case the γ-α transition occurs under pressure at this temperature.[101] Similar volume collapse transitions are observed under pressure in Pr and Gd (for a recent review, see Ref. 102). It is widely believed that these transitions arise from changes in the degree of $4f$ electron correlations, as is reflected in both the Mott transition[103] and the Kondo volume collapse (KVC)[104] models.

The Mott transition model envisions a change from itinerant, bonding character of the $4f$-

electrons in the α-phase to non-bonding, localized character in the γ-phase, driven by changes in the $4f$-$4f$ inter-site hybridization. Thus, as the ratio of the $4f$ Coulomb interaction to the $4f$-bandwidth increases, a Mott transition occurs to the γ-phase, similar to the Mott-Hubbard transition of the $3d$-electrons in V_2O_3 (Section 5).

The Kondo volume collapse[104] scenario ascribes the collapse to a strong change in the energy scale associated with the screening of the local $4f$-moment by conduction electrons (Kondo screening), which is accompanied by the appearance of an Abrikosov-Suhl-like quasiparticle peak at the Fermi level. In this model the $4f$-electron spectrum of Ce would change across the transition in a fashion very similar to the Mott scenario, i.e., a strong reduction of the spectral weight at the Fermi energy should be observed in going from the α- to the γ-phase. The subtle difference comes about by the γ-phase having metallic f-spectra with a strongly enhanced effective mass as in a heavy fermion system, in contrast to the f-spectra characteristic of an insulator in the case of the Mott scenario. The f-spectra in the Kondo picture also exhibit Hubbard side-bands not only in the γ-phase, but in the α-phase as well, at least close to the transition. While local-density and static mean-field theories correctly yield the Fermi-level peaks in the f-spectra for the α-phase, they do not exhibit such additional Hubbard side-bands, which is sometimes taken as characteristic of the "α-like" phase in the Mott scenario.[103] However, this behavior is more likely a consequence of the static mean-field treatment, as correlated solutions of both Hubbard and periodic Anderson models exhibit such residual Hubbard side-bands in the α-like regimes.[105]

Typically, the Hubbard model and the periodic Anderson model are considered as paradigms for the Mott and KVC model, respectively. Although both models describe completely different physical situations it was shown recently that one can observe a surprisingly similar behavior at finite temperatures: the evolution of the spectrum and the local magnetic moment with increasing Coulomb interaction show very similar features as well as, in the case of a periodic Anderson model with nearest neighbor hybridization, the phase diagram and the charge compressibility.[105,106] From this point of view the distinction between the two scenarios appears to be somewhat artificial, at least at temperatures relevant for the description of the α-γ transition.

For a realistic calculation of the cerium α-γ transition, we employ the full Hamiltonian calculation described in Sections 2.3, 2.4, and 2.5 where the one-particle Hamiltonian was calculated by LDA and the $4f$ Coulomb interaction U along with the associated $4f$ site energy shift by a constrained LDA calculation (for details of the two independent calculations presented in the current Section see Refs. 60, 61, 102 and Ref. 59). We have not included the spin-orbit interaction which has a rather small impact on LDA results for Ce, nor the intra-atomic exchange interaction which is less relevant for Ce as occupations with more than one $4f$-electron on the same site are rare [$J = 0$ in Eq. (13)]. Furthermore, the $6s$-, $6p$-, and $5d$-orbitals are assumed to be non-interacting in the formalism of Eq. (13), Section 2.4. Note, that the $4f$ orbitals are even better localized than the $3d$ orbitals and, thus, uncertainties in U and the 4f site energy [$\Delta\epsilon_d$ in (13)] are relatively small and would only translate into a possible volume shift for the α-γ-transition.

The LDA+DMFT(QMC) spectral evolution of the Ce $4f$-electrons is presented in Fig. 15. It shows similarities to V_2O_3 (Fig. 13, Section 5): At a volume per atom $V = 20\,\text{Å}^3$, Fig. 15 shows

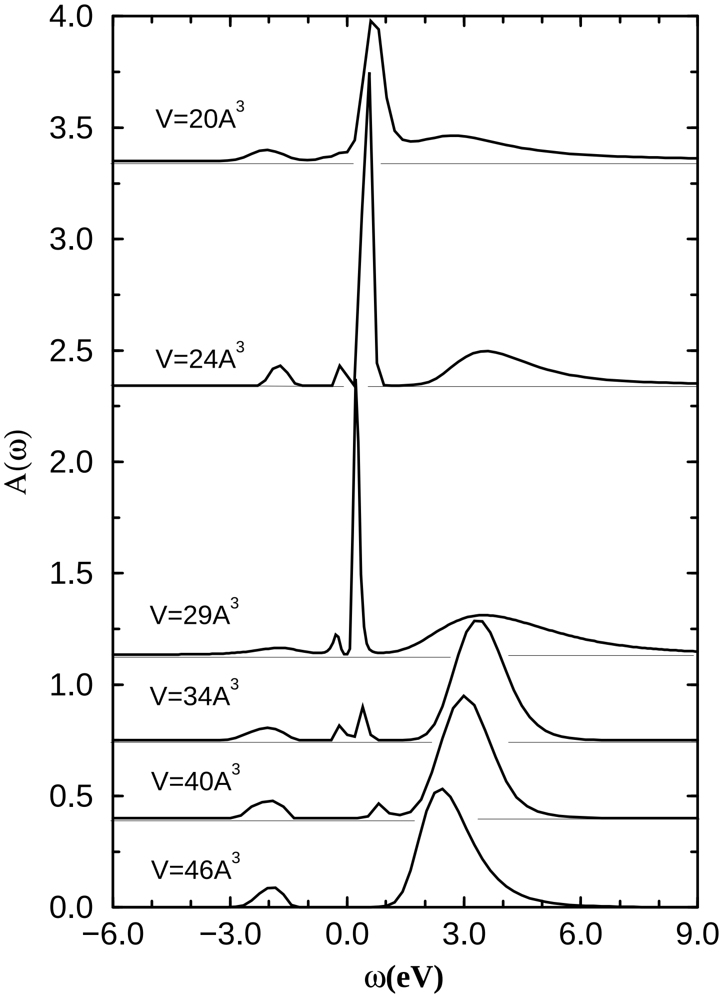


Figure 15: Evolution of the $4f$ spectral function $A(\omega)$ with volume at $T = 632\,\mathrm{K}$ ($\omega = 0$ corresponds to the chemical potential; curves are offset as indicated; $\Delta\tau = 0.11\mathrm{eV}^{-1}$). Coinciding with the sharp anomaly in the correlation energy (Fig. 16), the central quasiparticle resonance disappears, at least at finite temperatures [reproduced from Ref. 61].

that almost the entire spectral weight lies in a large quasiparticle peak with a center of gravity slightly above the chemical potential. This is similar to the LDA solution; however, a weak upper Hubbard band is also present even at this small volume. At the volumes 29 Å^3 and 34 Å^3 which approximately bracket the α-γ transition, the spectrum has a three peak structure. Finally, by $V = 46$ Å^3, the central peak has disappeared leaving only the lower and upper Hubbard bands. However, an important difference to V_2O_3 is that the *spd*-spectrum shows metallic behavior and, thus, cerium remains a metal throughout this transition monitored by a vanishing $4f$ quasiparticle resonance.

To study the energetic changes associated with the rapid change of the quasiparticle weight at the Fermi energy, we calculate the DMFT energy per site for the model Hamiltonian (13)

$$E_{\mathrm{DMFT}} = \frac{T}{N_k}\sum_{n\mathbf{k}\sigma}\mathrm{Tr}(H^0_{\mathrm{LDA}}(\mathbf{k})G_{\mathbf{k}}(i\omega_n))e^{i\omega_n 0^+} + U_f\, d. \tag{45}$$

Here, Tr denotes the trace over the 16 × 16 matrices, T the temperature, N_k the number of k points, $G_{\mathbf{k}}$ the Green function matrix w.r.t. the orbital indices, $H^0_{\mathrm{LDA}}(\mathbf{k})$ the LDA one-particle

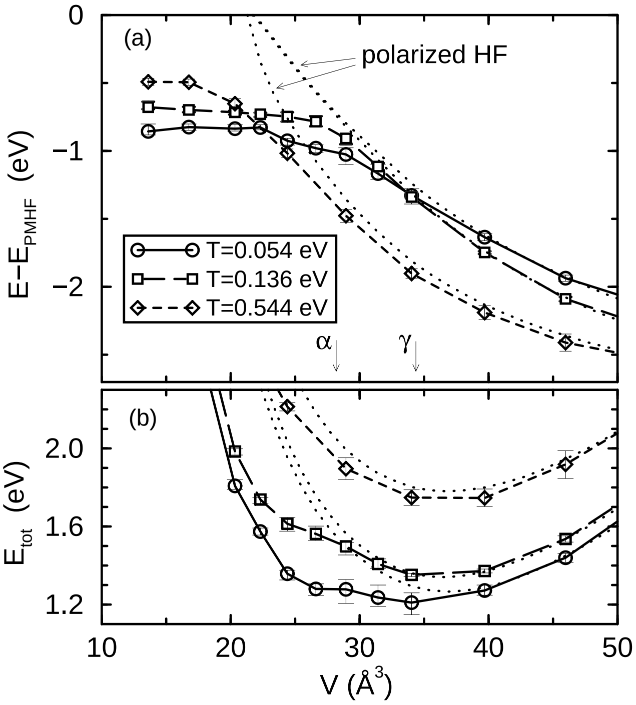


Figure 16: (a) Correlation energy $E_{\mathrm{DMFT}} - E_{\mathrm{PMHF}}$ as a function of atomic volume (symbols) and polarized HF energy $E_{\mathrm{AFHF}} - E_{\mathrm{PMHF}}$ (dotted lines which, at large V, approach the DMFT curves for the respective temperatures); arrows: observed volume collapse from the α- to the γ-phase. The correlation energy sharply bends away from the polarized HF energy in the region of the transition. (b) The resultant negative curvature leads to a growing depression of the total energy near $V = 26$–28 Å^3 as temperature is decreased, consistent with an emerging double well at still lower temperatures and thus the α-γ transition. The curves at $T = 0.544\,\mathrm{eV}$ were shifted downwards in (b) by $-0.5\,\mathrm{eV}$ to match the energy range [reproduced from Ref. 60].

matrix Eq. (15), and

$$d = \frac{1}{2}{\sum}'_{m\sigma,m'\sigma'} \langle \hat{n}_{ifm\sigma}\, \hat{n}_{ifm'\sigma'} \rangle \qquad (46)$$

is a generalization of the one-band double occupation for multi-band models.

Fig. 16a shows our calculated DMFT(QMC) energies E_{DMFT} as a function of atomic volume at three temperatures *relative* to the paramagnetic Hartree Fock (HF) energies E_{PMHF} [of the Hamiltonian (13)], i.e., the energy contribution due to *electronic correlations.* We also present the polarized HF energies which basically represent a (non-self-consistent) LDA+U calculation and reproduce E_{DMFT} at large volumes and low temperatures. With decreasing volume, however, the DMFT energies bend away from the polarized HF solutions. Thus, at $T = 0.054\,\mathrm{eV} \approx 600\,\mathrm{K}$, a region of negative curvature in E_{DMFT}–E_{PMHF} is evident within the observed two phase region (arrows).

Fig. 16b presents the calculated LDA+DMFT total energy $E_{\mathrm{tot}}(T) = E_{\mathrm{LDA}}(T) + E_{\mathrm{DMFT}}(T) - E_{\mathrm{mLDA}}(T)$ where E_{mLDA} is the energy of an LDA-like solution of the Hamiltonian (13).[107] Since both E_{LDA} and $E_{\mathrm{PMHF}} - E_{\mathrm{mLDA}}$ have positive curvature throughout the volume range considered, it is the negative curvature of the correlation energy in Fig. 16a which leads to the dramatic depression of the LDA+DMFT total energies in the range $V = 26$-28 Å^3 for decreasing

	α-Ce LDA+DMFT(QMC)	α-Ce LDA+DMFT(NCA)	α-Ce exp[108,109]	γ-Ce LDA+DMFT(QMC)	γ-Ce LDA+DMFT(NCA)	γ-Ce exp[108,109]
P_0	0.12 ± 0.03	0.126	0.1558	0.01 ± 0.02	0.0150	0.0426
P_1	0.77 ± 0.03	0.829	0.8079	0.94 ± 0.03	0.9426	0.9444
P_2	0.11 ± 0.01	0.044	0.0264	0.05 ± 0.01	0.0423	0.0131
n_f	0.99 ± 0.01	0.908	$0.8 \ldots 0.861$	1.04 ± 0.02	1.014	$0.971 \ldots 1$
T_K, [K]	≈ 2100	1000	$945 \ldots 2000$	n.a.	30	$60 \ldots 95$
χ, $[10^{-3} \frac{\text{emu}}{\text{mol}}]$	n.a.	1.08	$0.53 \ldots 0.70$	n.a.	24	$8.0 \ldots 12$

Table 1: Comparison between LDA+DMFT(QMC)[61] and LDA+DMFT(NCA)[59] calculated parameters for both α- and γ-phase and experimental values.[108,109] P_0, P_1 and P_2 are partial probabilities for an empty, singly and doubly occupied $4f$-state, n_f is the f-electron occupancy, T_K the estimated Kondo temperature, and χ the magnetic susceptibility.

temperature, which contrasts to the smaller changes near $V = 34\,\text{Å}^3$ in Fig. 16b. This trend is consistent with a double well structure emerging at still lower temperatures (prohibitively expensive for QMC simulations), and with it a first-order volume collapse. This is in reasonable agreement with the experimental volume collapse. Further physical quantities like the free energy and the specific heat are presented in Ref. 61. Also note that a similar scenario has been proposed recently for the δ-α transition in Pu on the basis of LDA+DMFT calculations,[57] which solves DMFT by an ansatz inspired by IPT and includes a modification of the DFT/LDA step to account for the density changes introduced by the DMFT.[58]

In the LDA+DMFT(QMC) and in a separate LDA+DMFT(NCA)[59] calculation for Ce, we have obtained a number of physical quantities for both phases which may be compared to experimental values. Various static properties extracted from the calculations and their counterparts extracted from experiments are collected in Table 1 and show an overall fair to good agreement in the tendencies and, except for the susceptibility, the absolute values. The differences between LDA+DMFT(QMC)[61] and LDA+DMFT(NCA)[59] are most likely due to the different method employed to solve the DMFT self-consistency equations. But also, difference in the LDA treatment and, for α-Ce, in the Coulomb interaction U might matter (in Ref. 59, U was assumed to be the same for α- and γ-Ce, whereas the *ab initio* determination of U in Ref. 102 which was employed in Refs. 60, 61 yield a slightly smaller U-value for α- than for γ-Ce). Since the calculation of the magnetic susceptibility χ in Ref. 59 was based on simplifying assumptions, the absolute numbers cannot be expected to match experiment. However, the general tendency and especially the ratio between α- and γ-Ce is in good agreement with experiment. It is interesting to note that the experiments predict a finite Kondo screening-scale for both phases, which actually would point toward the KVC scenario.

Finally, let us compare the spectral functions calculated with the LDA+DMFT(QMC) approach to experimental data.[110] The photoemission spectrum for α-Ce (upper part of Fig. 17) shows a main structure between 3 eV and 7 eV, which is attributed to $4f^2$ final state multiplets. In the calculated spectrum all excitations to $4f^2$ states are described by the featureless upper

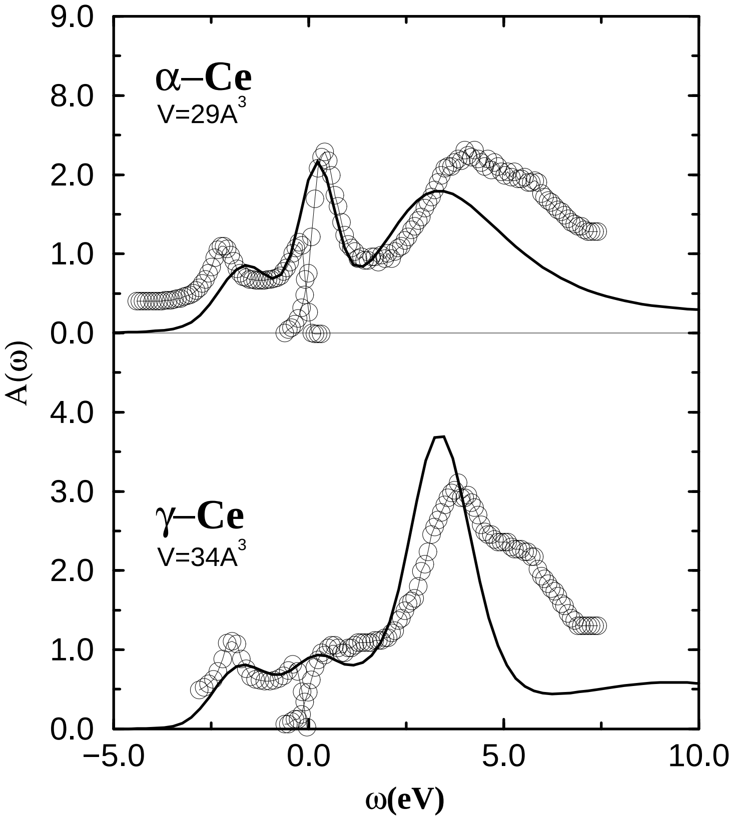


Figure 17: Comparison between combined photoemission[110] and BIS[111] experimental (circles) and theoretical LDA+DMFT(QMC) total spectra (solid line) for α- (upper part) and γ-Ce (lower part) at $T = 580\,\mathrm{K}$. The experimental and theoretical spectra were normalized and the theoretical curve was broadened with resolution width of 0.4 eV [reproduced from Ref. 61].

Hubbard band. As a consequence of the simplified interaction model all doubly occupied states are degenerate. This shortcoming in our calculation is responsible for the sharply peaked main structure. The neglected exchange interaction would produce a multiplet structure, which would be closer to the experiment. The calculated f-spectrum shows a sharp quasiparticle or Kondo resonance slightly above the Fermi energy, which is the result of the formation of a singlet state between f- and conduction states. We thus suggest that the spectral weight seen in the experiment is a result of this quasiparticle resonance. In the lower part of Fig. 17, a comparison between experiment and our calculation for γ-Ce is shown. The most striking difference between the lower and the upper part of Fig. 17 is the absence of the Kondo resonance in the γ-phase which is in agreement with our calculations. Nonetheless γ-Ce remains metallic with spectral weight arising from the *spd*-electrons at the Fermi energy. Altogether, one can say that the agreement with the experimental spectrum is very good, and comparable to the LDA accuracy for much simpler systems.

7 Conclusion and Outlook

At present LDA+DMFT is the only available *ab initio* computational technique which is able to treat correlated electronic systems close to a Mott-Hubbard MIT, heavy fermions, and f-electron materials. The physical properties of such systems are characterized by the correlation-induced generation of small, Kondo-like energy scales which are missing in the LDA and which require the application of genuine many-body techniques.

In this paper we discussed the set-up of the computational scheme LDA+DMFT which merges two non-perturbative, complementary investigation techniques for many-particle systems in solid state physics. LDA+DMFT allows one to perform *ab initio* calculations of real materials with strongly correlated electrons. Using the band structure results calculated within local density approximation (LDA) as input, the missing electronic correlations are introduced by dynamical mean-field theory (DMFT). On a technical level this requires the solution of an effective self-consistent, multi-band Anderson impurity problem by some numerical method (e.g. IPT, NCA, QMC). Comparison of the photoemission spectrum of $La_{1-x}Sr_xTiO_3$ calculated by LDA+DMFT using IPT, NCA, and QMC reveal that the choice of the evaluation method is of considerable importance. Indeed, only with the numerically exact QMC quantitatively reliable results are obtained. The results of the LDA+DMFT(QMC) approach were found to be in good agreement with the experimental photoemission spectrum of $La_{0.94}Sr_{0.06}TiO_3$.

We also presented results of a LDA+DMFT(QMC) study[48] of the Mott-Hubbard metal-insulator transition (MIT) in the paramagnetic phase of (doped) V_2O_3. These results showed a MIT at a reasonable value of the Coulomb interaction $U \approx 5\,\text{eV}$ and are in very good agreement with the experimentally determined photoemission and X-ray absorption spectra for this system, i.e., above *and* below the Fermi energy. In particular, we find a spin state $S = 1$ in the paramagnetic phase, and an orbital admixture of $e_g^\pi e_g^\pi$ and $e_g^\pi a_{1g}$ configurations, which both agree with recent experiments. Thus, LDA+DMFT(QMC) provides a remarkably accurate microscopic theory of the strongly correlated electrons in the paramagnetic metallic phase of V_2O_3.

Another material where electronic correlations are considered to be important is cerium. We reviewed our recent investigations of the Ce α-γ transition, based on LDA+DMFT(QMC)[60,61] and LDA+DMFT(NCA)[59] calculations. The spectral results and susceptibilities show the same tendency as seen in the experiment, namely a dramatic reduction in the size of the quasiparticle peak at the Fermi level when passing from the α- to the γ-phase. While we do not know at the moment whether the zero-temperature quasiparticle peak will completely disappear at an even larger volume (i.e., in a rather Mott-like fashion) or simply fade away continuously with increasing volume (i.e., in a more Kondo-like fashion), an important aspect of our results is that the rapid reduction in the size of the peak seems to coincide with the appearance of a negative curvature in the correlation energy and a shallow minimum in the total energy. This suggest that the electronic correlations responsible for the reduction of the quasiparticle peak are associated with energetic changes that are strong enough to cause a volume collapse in the sense of the Kondo volume collapse model,[104] or a Mott transition model[103] including electronic correlations.

We also discussed the embedding of LDA+DMFT in a spectral density functional theory, and extensions like self-consistent LDA+DMFT calculations, LDA+cluster DMFT, and GW+DMFT. These extensions are still work in progress which have been applied to model systems or, in the case of self-consistent LDA+DMFT, to Pu where a fast IPT-inspired DMFT solver has been employed.[57,58] A systematic analysis of the effect of these extensions in the context of realistic calculations is still mandatory and certainly depends on the system at hand. E.g., one would certainly expect the non-local correlations taken into account by cluster DMFT approaches to be much more important for effectively one- and two-dimensional systems than in three dimensions.

Another important aspect of future investigations is the calculation of other physical quantities. In the first LDA+DMFT publications, mainly the local spectral function (Green function) was calculated because it arises naturally in the DMFT self-consistency scheme. Nonetheless, in the near future more physical quantities will be calculated by LDA+DMFT: thermodynamic properties like the specific heat or entropy, which have been already calculated for f-electron systems but not yet for transition metal oxides; transport properties like the electrical, optical, and thermal conductivity; magnetic, orbital and other susceptibilities; calculations will also be performed within symmetry broken phases and phase diagrams will be obtained.

Physicists from two strong solid state communities, i.e., the DFT bandstructure and the many-body community, have finally joined forces to develop and apply LDA+DMFT. The outcome is a powerful tool for future investigations of electronic properties of real materials *with strong electronic correlations.*

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References

[1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, 4A, A1133 (1965); W. Kohn and L. J. Sham, Phys. Rev. A - Gen. Phys. **140**, 1133 (1965); L. J. Sham and W. Kohn, Phys. Rev. **145 N 2**, 561 (1966).

[3] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[4] T. C. Leung, X. W. Wang, and B. N. Harmon, Phys. Rev. B **37**, 384 (1988); J. Zaanen, O. Jepsen, O. Gunnarsson, A. T. Paxton, and O. K. Andersen, Physica C **153**, 1636 (1988); W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[5] L. F. Mattheiss, J. Phys.: Cond. Matt. **6**, 6477 (1994).

[6] K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMahan, R. T. Scalettar, Th. Pruschke, V. I. Anisimov, and D. Vollhardt, in *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, J. Grotendorst, D. Marks, and A. Muramatsu (ed.), NIC Series Volume 10, p. 175-209 (2002).

[7] A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar, to be published in *Electron Correlations and Materials Properties 2*, A. Gonis (ed.), Kluwer, New York; G. Kotliar and S. Savrasov, in *New Theoretical Approaches to Strongly Correlated Systems*, A. M. Tsvelik (ed.), Kluwer, New York, 2001, p. 259.

[8] M. Born and R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).

[9] M. Levy, Proc. Natl. Acad. Sci. (USA), **76**, 6062 (1979).

[10] L. Hedin and B. Lundqvist, J. Phys. C: Solid State Phys. **4**, 2064 (1971); U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. **5**, 1629 (1972).

[11] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[12] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983); O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[13] O. K. Andersen, T. Saha-Dasgupta, S. Ezhov, L. Tsetseris, O. Jepsen, R. W. Tank, C. Arcangeli, and G. Krier, Psi-k Newsletter 45, 86 (2001).

[14] E. Müller-Hartmann, Z. Phys. B **74**, 507 (1989); ibid. B **76**, 211 (1989).

[15] J. Wahle, N. Blümer, J. Schlipf, K. Held, and D. Vollhardt, Phys. Rev. B **58**, 12749 (1998).

[16] O. Gunnarson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).

[17] I. A. Nekrasov, K. Held, N. Blümer, A. I. Poteryaev, V. I. Anisimov, and D. Vollhardt, Euro. Phys. J. B **18**, 55 (2000).

[18] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).

[19] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991); V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Cond. Matter **9**, 767 (1997).

[20] V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, J. Phys. Cond. Matter **9**, 7359 (1997).

[21] A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B **57**, 6884 (1998).

[22] V. Drchal, V. Janiš, and J. Kudrnovský, in *Electron Correlations and Material Properties*, edited by A. Gonis, N. Kioussis, and M. Ciftan, Kluwer/Plenum, New York, 1999, p. 273.

[23] J. Lægsgaard and A. Svane, Phys. Rev. B **58**, 12817 (1998).

[24] Th. Wolenski, *Combining bandstructure and dynamical mean-field theory: A new perspective on* V_2O_3, Ph.D. Thesis, Universität Hamburg 1998 (Shaker Verlag, Aachen, 1999).

[25] M. B. Zölfl, Th. Pruschke, J. Keller, A. I. Poteryaev, I. A. Nekrasov, and V. I. Anisimov, Phys. Rev. B **61**, 12810 (2000).

[26] W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989).

[27] U. Brandt and C. Mielsch, Z. Phys. B **75**, 365 (1989); ibid. B **79**, 295 (1989); ibid. B **82**, 37 (1991).

[28] V. Janiš, Z. Phys. B **83**, 227 (1991); V. Janiš and D. Vollhardt, Int. J. Mod. Phys. **6**, 731 (1992).

[29] A. Georges and G. Kotliar, Phys. Rev. B **45**, 6479 (1992).

[30] M. Jarrell, Phys. Rev. Lett. **69**, 168 (1992).

[31] D. Vollhardt, in *Correlated Electron Systems*, edited by V. J. Emery, World Scientific, Singapore, 1993, p. 57.

[32] Th. Pruschke, M. Jarrell, and J. K. Freericks, Adv. in Phys. **44**, 187 (1995).

[33] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[34] P. W. Anderson, in *Moment formation in solids*, edited by W. J. L. Buyers, Plenum Press, New York and London, 1984, p. 313.

[35] W. Negele and H. Orland, *Quantum Many-Particle Systems*, Addison-Wesley, New York, 1987.

[36] H. Keiter and J. C. Kimball, Phys. Rev. Lett. **25**, 672 (1970); N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B **36**, 2036 (1987).

[37] Th. Pruschke and N. Grewe, Z. Phys. B **74**, 439 (1989).

[38] Th. Pruschke, D. L. Cox, and M. Jarrell, Phys. Rev. B **47**, 3553 (1993).

[39] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986); M. Jarrell, Phys. Rev. Lett. **69**, 168 (1992); M. Rozenberg, X. Y. Zhang, and G. Kotliar, Phys. Rev. Lett. **69**, 1236 (1992); A. Georges and W. Krauth, Phys. Rev. Lett. **69**, 1240 (1992); M. Jarrell, in *Numerical Methods for Lattice Quantum Many-Body Problems*, edited by D. Scalapino, Addison Wesley, 1997.

[40] M. J. Rozenberg, Phys. Rev. B **55**, R4855 (1997).

[41] J. E. Han, M. Jarrell, and D. L. Cox, Phys. Rev. B **58**, R4199 (1998).

[42] K. Held and D. Vollhardt, Euro. Phys. J. B **5**, 473 (1998).

[43] M. Caffarel and W. Krauth, Phys. Rev. Lett. **72**, 1545 (1994).

[44] R. Bulla, Adv. Sol. State Phys. **46**, 169 (2000).

[45] H. Kajueter and G. Kotliar, Int. J. Mod. Phys. **11**, 729 (1997).

[46] M. I. Katsnelson and A. I. Lichtenstein, J. Phys. Cond. Matter **11**, 1037 (1999).

[47] M. I. Katsnelson and A. I. Lichtenstein, Phys. Rev. B **61**, 8906 (2000).

[48] K. Held, G. Keller, V. Eyert, V. I. Anisimov, and D. Vollhardt, Phys. Rev. Lett. **86**, 5345 (2001).

[49] M. S. Laad, L. Craco, and E. Müller-Hartmann, cond-mat/0211210.

[50] I.A. Nekrasov, G. Keller, D.E. Kondakov, A.V. Kozhevnikov, Th. Pruschke, K. Held, D. Vollhardt, and V.I. Anisimov, cond-mat/0211508; A. Liebsch, cond-mat/0301537.

[51] I.A. Nekrasov, Z.V. Pchelkina, G. Keller, Th. Pruschke, K. Held, A. Krimmel, D. Vollhardt, and V.I. Anisimov, Phys. Rev. B **67**, 85111 (2003).

[52] A. Liebsch and A. I. Lichtenstein, Phys. Rev. Lett. **84**, 1591 (2000); A. Liebsch, cond-mat/0301536.

[53] V. I. Anisimov, I. A. Nekrasov, D. E. Kondakov, T. M. Rice, and M. Sigrist, Eur. Phys. J. B **25**, 191-201 (2002).

[54] L. Craco, M. S. Laad, and E. Müller-Hartmann, cond-mat/0209132.

[55] A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar Phys. Rev. Lett. **87**, 67205 (2001).

[56] S. Biermann, A. Dallmeyer, C. Carbone, W. Eberhardt, C. Pampuch, O. Rader, M. I. Katsnelson, and A. I. Lichtenstein, cond-mat/0112430.

[57] S. Y. Savrasov, G. Kotliar, and E. Abrahams, Nature **410**, 793 (2001).

[58] S. Y. Savrasov and G. Kotliar, cond-mat/0106308.

[59] M. B. Zölfl, I. A. Nekrasov, Th. Pruschke, V. I. Anisimov, and J. Keller, Phys. Rev. Lett. **87**, 276403 (2001).

[60] K. Held, A. K. McMahan, and R. T. Scalettar, Phys. Rev. Lett. **87**, 276404 (2001).

[61] A. K. McMahan, K. Held, and R. T. Scalettar, Phys. Rev. B **67**, 75108 (2003).

[62] W. Weber, J. Bünemann, and F. Gebhard, in *Band-Ferromagnetism*, edited by K. Baberschke, M. Donath, and W. Nolting, Lecture Notes in Physics, Vol. 580 (Springer, Berlin, 2001), p. 9; J. Bünemann, F. Gebhard, W. Weber, Phys. Rev. B **57**, 6896 (1998).

[63] M. Suzuki, Prog. Theor. Phys. **56**, 1454 (1976)

[64] One limitation of QMC is that it is very difficult to deal with the spin-flip term of the Hund's rule coupling because of a "minus-sign problem" which arises in a Hubbard-Stratonovich decoupling of this spin-flip term, see K. Held, *Untersuchung korrelierter Elektronensysteme im Rahmen der Dynamischen Molekularfeldtheorie*, Ph.D. thesis, Universität Augsburg 1999 (Shaker Verlag, Aachen, 1999). In the particle-hole symmetric case another decoupling scheme which includes the spin-flip term is possible without "minus-sign problem", see Y. Motome and M. Imada, J. Phys. Soc. Jap. **66**, 1872 (1997).

[65] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[66] M. Jarrell and J. E. Gubernatis, Physics Reports **269**, 133 (1996).

[67] E. Müller-Hartmann, Z. Phys. B **57**, 281 (1984).

[68] G. Kotliar, Physica B 259-261, 711 (1999). R. Chitra and G. Kotliar, Phys. Rev. B **62**, 12715 (2000).

[69] R. Fukuda, T. Kotani, and S. Yokojima, Prog. Theory Phys. **92**, 833 (1994); R. Fukuda et al., Prog. Theory Phys. Suppl. **121**, 1 (1996).

[70] G. Kotliar, S. Y. Savrasov, G. Pálsson, and G. Biroli, Phys. Rev. Lett. **87**, 186401 (2001); G. Biroli and G. Kotliar, Phys. Rev. B **65**, 155112 (2002).

[71] A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B **62**, 9283 (2000).

[72] M. Potthoff, M. Aichhorn, and C. Dahnken, preprint.

[73] M. H. Hettler, A. N. Tahvildar-Zadeh, and M. Jarrell, Phys. Rev. B **58**, 7475 (1998); M. H. Hettler, M. Mukherjee, M. Jarrell, and H. R. Krishnamurthy, Phys. Rev. B **61**, 12739 (2000). Note, that one of the implementations in Ref. 71 is equivalent to DCA.

[74] A. Schiller and K. Ingersent, Phys. Rev. Lett. **75**, 113 (1995); G. Zaránd, D. L. Cox, and A. Schiller, Phys. Rev. B **62**, 16227 (2000).

[75] Th. Maier, M. Jarrell, Th. Pruschke, and J. Keller, Phys. Rev. Lett. **85**, 1524 (2000); Eur. Phys. J. B **13** 613 (2000); C. Huscroft, M. Jarrell, Th. Maier, S. Moukouri, and A. N. Tahvildarzadeh, Phys. Rev. Lett. **86**, 139 (2001).

[76] L. Hedin, Phys. Rev. **139**, A796 (1965); F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).

[77] P. Sun and G. Kotliar, Phys. Rev. B **66**, 85120 (2002); S. Biermann, F. Aryasetiawan, and A. Georges, cond-mat/0207419.

[78] D. A. MacLean, H.-N. Ng, and J. E. Greedan, J. Solid State Chem. **30**, 35 (1979).

[79] M. Eitel and J. E. Greedan, Journal of the Less-Common Metals **116**, 95 (1986).

[80] J. P. Gopel, J. E. Greedan, and D. A. MacLean, J. Solid State Chem. **43**, 244 (1981).

[81] Y. Okimoto, T. Katsufuji, Y. Okada, T. Arima, and Y. Tokura, Phys. Rev. B **51**, 9581 (1995).

[82] W. Heindl, Th. Pruschke, and J. Keller, J. Phys. – Condens. Matter **12**, 2245 (2000).

[83] At present, QMC simulations of the DMFT equations are not feasible at the experimental temperature (80K). We note, however, that no intrinsic temperature dependence was observed in the experiment,[84] at least up to room temperature.

[84] A. Fujimori *et al*, Phys. Rev. Lett. **69**, 1796 (1992). A. Fujimori *et al*, Phys. Rev. B **46**, 9841 (1992). A qualitatively *and* quantitatively similar spectrum was obtained recently by T. Yoshida, A. Ino, T. Mizokawa, A. Fujimori, Y. Taguchi, T. Katsufuji, and Y. Tokura, Europhys. Lett. **59**, 258 (2002), with an experimental energy resolution of only 30 meV. One may suppose, however, that broadening effects due to the polycrystalline nature of the sample and surface effects are, then, larger than the instrumental resolution.

[85] B. Keimer, D. Casa, A. Ivanov, J.W. Lynn, M. v. Zimmermann, J.P. Hill, D. Gibbs, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. **85**, 3946 (2000).

[86] N. F. Mott, Rev. Mod. Phys. **40**, 677 (1968); *Metal-Insulator Transitions* (Taylor & Francis, London, 1990); F. Gebhard, *The Mott Metal-Insulator Transition* (Springer, Berlin, 1997).

[87] D. B. McWhan *et al.*, Phys. Rev. B **7**, 1920 (1973).

[88] J. Hubbard, Proc. Roy. Soc. London Ser. A **276**, 238 (1963); **277**, 237 (1963); **281**, 401 (1964).

[89] W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).

[90] G. Moeller, Q. Si, G. Kotliar, and M. Rozenberg, Phys. Rev. Lett. **74**, 2082 (1995); J. Schlipf, M. Jarrell, P. G. J. van Dongen, N. Blümer, S. Kehrein, Th. Pruschke, and D. Vollhardt, Phys. Rev. Lett. **82**, 4890 (1999); M. J. Rozenberg, R. Chitra, and G. Kotliar, Phys. Rev. Lett. **83**, 3498 (1999); R. Bulla, Phys. Rev. Lett. **83**, 136 (1999); R. Bulla, T. A. Costi, and D. Vollhardt, Phys. Rev. B **64**, 45103 (2001); J. Joo and V. Oudovenko, Phys. Rev. B **64**, 193102 (2001); N. Blümer, *Mott-Hubbard Metal-Insulator Transition and Optical Conductivity in High Dimensions*, Ph.D. thesis, Universität Augsburg 2002.

[91] P. D. Dernier, J. Phys. Chem. Solids **31**, 2569 (1970).

[92] Use of the crystal structure of Cr-doped V_2O_3 for the insulating phase of pure V_2O_3 is justified by the observation that Cr-doping is equivalent to the application of (negative) pressure.

[93] M. Schramme, Ph.D. thesis, Universität Augsburg 2000 (Shaker Verlag, Aachen, 2000); M. Schramme *et al.* (unpublished).

[94] S.-K. Mo, J. D. Denlinger, H.-D. Kim, J.-H. Park, J. W. Allen, A. Sekiyama, A. Yamasaki, K. Kadono, S. Suga, Y. Saitoh, T. Muro, P. Metcalf, G. Keller, K. Held, V. Eyert, V. I. Anisimov, and D. Vollhardt, cond-mat/0212110.

[95] O. Müller, J. P. Urbach, E. Goering, T. Weber, R. Barth, H. Schuler, M. Klemm, S. Horn, and M. L. denBoer, Phys. Rev. B **56**, 15056 (1997).

[96] J.-H. Park, L. H. Tjeng, A. Tanaka, J. W. Allen, C. T. Chen, P. Metcalf, J. M. Honig, F. M. F. de Groot, and G. A. Sawatzky, Phys. Rev. B **61**, 11 506 (2000).

[97] D. J. Arnold and R. W. Mires, J. Chem. Phys. **48**, 2231 (1968).

[98] C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B **18**, 4945 (1978); **18**, 4967 (1978); **18**, 5001 (1978).

[99] M. J. Rozenberg, G. Kotliar, H. Kajueter, G. A. Thomas, D. H. Rapkine, J. M. Honig, and P. Metcalf, Phys. Rev. Lett. **75**, 105 (1995).

[100] *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider Jr. and L. R. Eyring (North-Holland, Amsterdam, 1978); in particular, D. G. Koskenmaki and K. A. Gschneider Jr., *ibid*, p.337.

[101] J. S. Olsen, L. Gerward, U. Benedict, and J.-P. Itié, Physica **133B**, 129 (1985).

[102] A. K. McMahan, C. Huscroft, R. T. Scalettar, and E. L. Pollock, J. Comput.-Aided Mater. Design **5**, 131 (1998).

[103] B. Johansson, Philos. Mag. **30**, 469 (1974); B. Johansson, I.A. Abrikosov, M. Aldén, A. V. Ruban, and H.L. Skriver Phys. Rev. Lett. **74**, 2335 (1995).

[104] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106, (1982); J. W. Allen and L. Z. Liu, Phys. Rev. B **46**, 5047, (1992); M. Lavagna, C. Lacroix, and M. Cyrot, Phys. Lett. **90A**, 210 (1982).

[105] K. Held, C. Huscroft, R.T. Scalettar, and A.K. McMahan, Phys. Rev. Lett. **85**, 373 (2000); see also C. Huscroft, A. K. McMahan, and R. T. Scalettar, Phys. Rev. Lett. **82**, 2342 (1999).

[106] K. Held and R. Bulla, Eur. Phys. J. B **17**, 7 (2000).

[107] We solve self-consistently for n_f using a $4f$ self energy $\Sigma = U_f(n_f - \frac{1}{2})$, and then remove this contribution from the eigenvalue sum to get the kinetic energy. The potential energy is taken to be $\frac{1}{2}U_f n_f(n_f - 1)$.

[108] L. Z. Liu, J. W. Allen, O. Gunnarsson, N. E. Christensen, and O. K. Andersen, Phys. Rev. B **45,** 8934 (1992).

[109] A. P. Murani, Z. A. Bowden, A. D. Taylor, R. Osborn, and W. G. Marshall, Phys. Rev B **48,** 13981 (1993).

[110] D. M. Wieliczka, C. G. Olson, and D. W. Lynch, Phys. Rev. B **29,** 3028 (1984).

[111] E. Wuilloud, H. R. Moser, W. D. Schneider, and Y. Baer, Phys. Rev. B **28,** 7354 (1983).