Ψ_k Newsletter

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

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Contents

1 Editorial

We start this newsletter with a short, summarizing report on the Psi-k2005 Conference by its chairman, Risto Nieminen. This is followed by an announcement of celebrations in Trieste to mark 20 years of Car-Parrinello. Then we have a brief information on a prestigeous EURYI award and its this year recipients. In the ESF Programme section we have information on how to subscribe to the ESF WG1 (GW+TDDFT) mailing list, followed by reports on two fairly recent workshops. In the section of the UK's CCP9 programme there is an announcement of a one-day meeting at Daresbury Laboratory on "Topics in Nanomagnetism". A detailed report of the NANOQUANTA network on their meeting on GW topics is placed right after the CCP9 announcement. Several workshop/meeting and available position announcements can be found in their respective sections, followed by abstracts of recent or newly submitted papers. A new journal is announced in the section "Presenting Other Initiatives", which is followed by the scientific highlight of the month. The latter is by Simone Raugei and Paolo Carloni (SISSA) on "Ab Initio Modeling of Biological Systems". For more details please check the table of contents of the newsletter.

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

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

The above contains information on the Psi-k 2005 workshops and hands-on courses (subject to funding). In these pages you 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@dl.ac.uk	**messages to the coordinators, editor & newsletter**
psik-network@dl.ac.uk	**messages to the whole Ψ_k community**

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2 General News

2.1 Summary Report on Psi-k2005 Conference in Schwäbisch Gmünd

The Psi-k Community convened to its third General Conference in Schwäbisch Gmünd, Germany, during September 17-21, 2005.

More than 560 scientists, representing 33 countries, from physics, chemistry, materials science, geophysics and biology gathered to survey and discuss the latest developments in the field of electronic structure theory and calculations, in the wide sense of the concept. The topics covered a huge selection of topics in condensed-matter and materials physics, ranging from new semiconductors to high-temperature superconductors, from magnetism to biomolecules, from surfaces and interfaces to geological and planetary sciences, etc.

The programme of the event consisted of four plenary sessions, 34 scientific sessions (running three in parallel) with 93 invited and 124 contributed oral presentations, and two poster sessions with more than 260 contributions.

The complete collection of abstracts is available at

http://www.fyslab.hut.fi/psik2005/psikbook.pdf

The conference carried the motto ”Towards ab initio materials design” of the European Science Foundation (ESF) Programme sponsoring it. This underlines the importance of the field to the development of nanosciences and nanotechnologies, where atomic-scale control is applied to achieve functional properties for new materials and devices, applied for example in information technology. The research also enables better understanding of, for example, the behaviour of biological processes, and matter under extreme conditions.

Looking back at the evolution of the field in view of the Psi-k Conferences, the progress has been spectacular indeed. From the roots in ”band structure calculations” the community has taken major steps to tackle complex many-electron problems beyond mean-field theories, and to apply the methods to an astounding array of real-world problems with demonstrated industrial relevance. An important factor in this progress has been the explosive increase in computer power. However, it is the ambitious and unprejudiced development and implementation of new theoretical and computational ideas, coupling electronic structure to dynamical and kinetic processes, that has made this possible. In my opinion, we are witnessing a paradigm shift in computational materials sciences.

Risto Nieminen
Psi-k2005 Chairman

2.2 20 Years of Car-Parrinello

November 25, 2005, University of Trieste, Aula Magna

The first Car-Parrinello simulation ran in 1985 in the Miramare building of the University of Trieste. The University will then celebrate the anniversary on Friday, November 25, with a scientific symposium and with **a Laurea honoris causa in Physics bestowed upon Roberto Car**. It is also noteworthy that Roberto Car is a native of Trieste, and that the event happens to fall within the Year of Physics.

Preliminary announcement

SYMPOSIUM: "Computer simulations: from physics to nanoscience"
November 25, 8:45, University of Trieste, Aula Magna.

Speakers (titles to be announced):

Alfonso Baldereschi, University of Trieste

Giulia Galli, University of California at Davis

Matthias Scheffler, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Michele Parrinello, ETH (Swiss Federal Inst. of Technology), Zurich and Lugano

CEREMONY: Laurea honoris causa bestowed upon Roberto Car November 25, 16:00, University of Trieste, Aula Magna.

2.3 Prestigeous EURYI Award

Two young people (emerging leaders) of our community got the prestigeous EURYI award.

About to enter its third year, EURYI - the European Young Investigator Awards scheme - is designed to attract outstanding young scientists from any country in the world to create their own research teams at European research centres. Most awards are between ∼1,000,000 and ∼1,250,000 EUR, and comparable in size to the Nobel Prize.

These young people are Angelos Michaelides (FHI Berlin) and Dario Alfe (London).

More information on Angelos you can find at

`http://www.mpg.de/bilderBerichteDokumente/dokumentation/pressemitteilungen/2005/pressemitteilung200508041/index.html`

while on Dario at

`http://chianti.geol.ucl.ac.uk/~dario/` .

More information about the EURYI award is available at

`http://www.esf.org/esf_pressarea_page.php?language=0&section=6&year=2005&newsrelease=92`

3 News from the ESF Programme

"Towards Atomistic Materials Design"

3.1 Participation in ESF WG1: GW+TDDFT

Following some questions during the Psi-k2005 Conference, we would like to remind you that sometime ago a mailing list for people interested in the activities of the ESF WG1 was created. For more information including registration to the mailing list you can go directly to

http://dipc.ehu.es/Psi-K/

where regularly we update all the activities of the WG1 including meetings, workshops, relations with other networks and internal communication between members of the WG1.

All this is accessible from the main psik web page

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

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3.2 Reports on ESF Workshops/Conferences

3.2.1 Report on ESF Workshop: Hands-on Tutorial course on LDA+DMFT

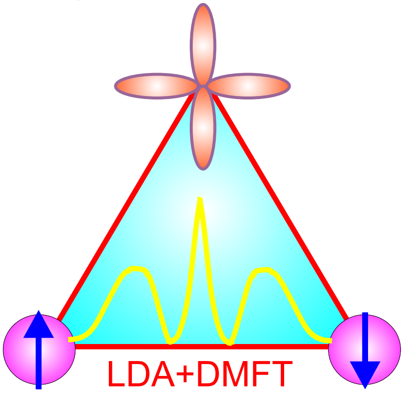
Institute of Theoretical Physics, University of Hamburg

May 17-20, 2005

ESF program 'Towards Atomistic Materials Design', RTN f-electron systems and University of Hamburg

Alexander Lichtenstein
University of Hamburg

`http://www.physnet.uni-hamburg.de/hp/alichten/Hands-on_Course_LDA+DMFT.htm`



The first hands on course on LDA+DMFT method was held in Hamburg, Germany, May 17-20, 2005. The scientific program covered nine invited talks and was attended by 50 participants. The purpose of this workshop was to offer an comprehensive theoretical introduction to the LDA+DMFT scheme and arrange a detailed practical calculations of real correlated systems using multi-band QMC code. The program was consists of the 9 two hour lectures given by experts in the LDA+DMFT field. The general introduction lectures on the DMFT scheme by Prof. D. Vollhardt (Augsburg) and on the NMTO scheme by Prof. O. K. Andersen (Stuttgart) give extended overview of the new fields in theory of electronic correlations and tight-binding description of complex solids. The detailed practical lectures by Dr. A. Poteryaev (Paris) on implementation of the LDA+DMFT method and Dr. E. Pavarini (Pavia) on the first-principle NMTO TB-Hamiltonoian for the DMFT scheme have a purpose to teach all technical know-how of LDA+DMFT scheme. This two lectures were followed by practical hands-on courses in computer class on the DMFT multiband QMC approach (Dr. Poteryaev) and NMTO-TB Hamiltonian scheme (Dr. E. Pavarini). All participants have possibilities to examine the state-of-the art computer code for tight-binding Wanier-like function in the solids and LDA+DMFT calculations within the Quantum Monte -Carlo for realistic perovskite systems ($LaTiO_3$ and $LaMnO_3$).

The new developments in the LDA+DMFT field were discussed in the lectures of Dr. K. Held (Stuttgart) on the projective multiband QMC for LDA+DMFT scheme for zero temperature calculations, Prof. S. Biermann (Paris) on GW+DMFT method for the first-principal investigation of screened Coulomb interactions and Prof. H. Ebert (Munchen) on LDA+DMFT calculation in the KKR scheme. Finally an important new type of impurity solver was discussed in the lecture of Prof. A. Rubtsov (Moswcow) on continuous QMC for finite fermionic system was followed by practical hands-on course on CT-QMC for DMFT scheme.

The mini-conference of the RTN program on f-electron focus on the recent progress in the LDA+DMFT investigation of different correlated materials.

The PDF-file of the lectures can be downloaded from the WWW-page of the workshop.

All the computer codes are available on the request:

NMTO - O.Jepsen@fkf.mpg.de

LDA+DMFT - Alexander.Poteryaev@cpht.polytechnique.fr

CT-QMC - alex@shg.phys.msu.su or www.ct-qmc.ru

Programme

Time	18-th May, Wednesday
09 – 00	D. Vollhardt (Augsburg)
	Electronic Correlations in Solids: From simple models to real materials
11 – 00	O. K. Andersen (Stuttgart)
	Introduction to the NMTO method
14 – 00	A. Poteryaev (Paris)
	Implementation of LDA+DMFT scheme
16 – 00	Tutorial on the LDA+DMFT
Time	19-th May, Thursday
09 – 00	A. Lichtenstein (Hamburg)
	Introduction to Spectral Density Functional and Cluster-DMFT
11 – 00	K. Held (Stuttgart)
	Projective multiband QMC for LDA+DMFT
14 – 00	E. Pavarini (Pavia)
	First-principle NMTO TB-Hamiltonian for DMFT
16 – 00	Tutorial on the NMTO-TB
Time	20-th May, Friday
09 – 00	S. Biermann (Paris)
	From LDA+DMFT to GW+DMFT approach
11 – 00	H. Ebert (Munich)
	LDA+DMFT in the KKR scheme
14 – 00	A. Rubtsov (Moscow)
	Continuous time QMC for fermions
16 – 00	Tutorial on the CT-QMC

Mini-conference

Time	17-th May, Wednesday
14 – 00	M. Katsnelson (Nijmegen)
	Local Perturbative Approach to Electronic Structure of Actinide Systems
14 – 30	L. Chioncel (Graz)
	Variational Cluster Perturbation Theory for Electronic Structure Calculations
15 – 00	J. Minar (Munich)
	Spectroscopies of Correlated Systems: KKR+DMFT approach
15 – 30	I. Nekrasov (Ekaterinburg)
	Pseudogap in Strongly Correlated Metals: A generalized DMFT approach
16 – 00	F. Lechermann (Paris)
	Fermi-Surface Deformations in Strongly Correlated Metals

Outline of the Lectures

Electronic Correlations in Solids: From simple models to real materials

D. Vollhardt

University of Augsburg, Germany

- Correlations
- Correlated Electron Materials
- Models approach - Single impurity physics - Dynamical Mean-Field Theory
- LDA+DMFT - Application to real material: (Sr,Ca)VO$_3$, V$_2$O$_3$, Ni
- Current developments and Perspectives

`http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Vollhardt_LDA+DMFT.pdf`

Downfolding, NMTO's and Wannier functions

O.K. Andersen

Max-Planck-Institute for Solid State Research, Stuttgart

- Bands & Bonds in Graphite
- TB model for the six π-electron in benzene
- Transition-metal oxides
- LDA+DMFT - Application to real material: (Sr,Ca)VO$_3$, V$_2$O$_3$, Ni
- NMTO-Wannier functions

`www.physnet.uni-hamburg.de/hp/alichten/lectures/OKA_NMTO.pdf`

Implementation of LDA+DMFT scheme

A. Poteryaev

Centre de Physique Theorique Ecole Polytechnique, Palaiseau, France

- DMFT for real systems
- Local Green function
- Hirsch QMC for impurity problem
- Examples

- The LDA+DMFT package

`http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Poteryaev_QMC.pdf`

Introduction to Spectral Density Functional and C-DMFT

A. Lichtenstein
University of Hamburg, Germany

- Strong correlations in real systems
- Functionals: MFT- DFT- DMFT
- Exchange Interactions and DMFT-Functional
- Transition Metals
- Cluster DMFT scheme
- Non-local effects in TMO

`http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Lichtenstein_SDF.pdf`

Projective QMC a new route to T=0 K

Held
Max-Planck-Institute for Solid State Research, Stuttgart

- Motivation
- Projective quantum Monte Carlo (PQMC) method
- One-band Hubbard model
- Two-band Hubbard model
- DCA (PQMC) study of the t-t_0 Hubbard model

`http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Held_PQMC.pdf`

First principles NMTO Hamiltonians for DMFT

E. Pavarini
University of Pavia, Italy

- From ab-initio to many-body models
- Realistic many-body models and the NMTO downfolding method
- NMTO Hamiltonians for DMFT
- 3d^1 perovskites

http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Pavarini_NMTO+DMFT.pd

From LDA+DMFT to GW+DMFT

S. Biermann
Centre de Physique Theorique Ecole Polytechnique, Palaiseau, France

- Reminder: impurity physics = the heart of DMFT
- Discussion of some practical issues in the context of LDA+DMFT (impurity solvers, analytical continuation ...)
- Which conceptual points to be aware of? correlated vs. uncorrelated orbitals, Hubbard-U, double counting)
- Some perspectives to go beyond LDA+DMFT (GW+DMFT)

http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Biermann_GW.pdf

Combination of the KKR-method and the DMFT

H. Ebert *University of Minich, Germany*

- Why KKR ?
- The Munich SPR-KKR package
- The SPR-KKR method
- Combination of KKR and DMFT
- Results for transition metal systems

http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Ebert_KKR+DMFT.pdf

Continuous time QMC for fermions

A. Rubtsov
Moscow State University, Russia

- Mathematics behind Monte-Carlo methods
- Series Expansion in interaction representation
- Random walk in K-space
- Worked example: DMFT on the Bethe lattice
- Complexity of the algorithm
- The CT-QMC package

`http://www.physnet.uni-hamburg.de/hp/alichten/lectures/Rubtsov_CTQMC.pdf`

List of participants

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3.2.2 Report on Joint CECAM-Psi-k Workshop on the Anomalous Hall Effect

Joint CECAM-Psi-k Workshop at CECAM, Lyon,
July 4 to July 6 2005

The anomalous Hall effect:
Recent advances via the geometric phase approach

Foreword

Other documentation about this event, more comprehensive than the present report, is available online at the URL `http://www.cecam.fr/`, under the item "Past workshops". In particular, the full participants' list, as well as the set of abstracts, are posted at the workshop website.

Summary (by R. Resta)

There have been sweeping advances since 2002 in understanding and computing the anomalous Hall effect (AHE) from first principles. The Hall resistivity of ferromagnets has an ordinary contribution (proportional to the external magnetic field strength), and an anomalous contribution (often assumed proportional to the sample magnetization). The phenomenon of AHE was discovered by E.R. Hall in 1881, shortly after his discovery of the normal effect. Nonetheless its interpretation has been controversial until recently. It is by now clear that the AHE is dominated by band-structure effects and can be computed as a suitable Berry phase. Other closely related, and equally controversial issues, concern the spin Hall effect, and orbital magnetization in extended systems. All of these issues have possible relevant implications for spintronics applications.

The above topics have been thoroughly and lively discussed in the workshop. Besides the "formal" presentations, an important part of the meeting has been in the long discussions, augmented with a few informal short presentations. We have gathered in Lyon 21 condensed matter theorists (plus a senior experimentalist), chosen among those who have in the past contributed significant advances in understanding and computing: electric polarization, orbital magnetization, anomalous Hall effect, quantum Hall effect, and Berry phases. Notably, we included scientists from the computational electronic-structure community, as well as scientists from a wider theoretical-physics community. It is remarkable that, while the preliminary participants' list was built on the basis of a generic cultural interest, some people in this list started working more specifically on the workshop topics only *after* the workshop was proposed and approved.

Given the nature of the event, most participants were senior ones, where some junior collaborators of the senior participants attended as well. Two young US participants profited of the NSF support under the CECAM-NSF agreement.

Some participants, including the most seniors of them, sent a feedback of real enthusiasm. It is remarkable that—despite the partial support available under the CECAM rules—almost one half of the participants travelled from overseas (USA, Japan, Taiwan) expressly for this very short event.

The success of the workshop owes to two main features. (1) Timeliness, demonstrated by the fact that a large number of important papers (e.g. PRLs), and preprints posted on the web, have appeared *after* the workshop was proposed and approved. (2) By means of participants' selection, care was taken to foster the interaction between physicists belonging to different communities: quantum-Hall (mostly analytical approach) and electronic structure (mostly computational approach).

Final programme

MONDAY, JULY 4th

09:00 09:30	Gathering at CECAM & starting some administrative work
09:30 10:30	Patrick Bruno - Anomalous Hall Effect in Ferromagnets
11:30 12:00	AM Duncan Haldane - Berry Phase Theory of the Anomalous Hall Effect
14:00 15:00	David Vanderbilt - Berry Phase Theory of Charge Effects in Insulators
15:00 15:15	Davide Ceresoli - Orbital Magnetization in Extended Systems: Theory
15:15 15:30	Timo Thonhauser - Orbital Magnetization in Extended Systems: Numerics and Results
16:00 16:30	Qian Niu - Berry phase correction to electron density of states in solids
16:30 16:50	Francesco Mauri - Pseudopotential Hamiltonian in Magnetic field: the orbital magnetism within a pseudopotential framework
16:50 onwards	Panel discussion on open issues on orbital magnetism (Mauri, Niu, Resta, Vanderbilt.....)

TUESDAY, JULY 5th

09:00 10:00	Allan MacDonald - Spin Hall Effect
10:00 10:30	Charles Kane - The Quantum Spin Hall Effect
11:00 11:30	Guang-Yu Guo - Ab initio calculation of spin Hall effect in

semiconductors and anomalous Hall effect in ferromagnetic insulators

11:30 12:00 Tomas Jungwirth and Jairo Sinova - Spin Hall Effect in the mesoscopic regime

14:00 14:30 Qian Niu - On A Proper Definition of Spin Current

14:30 15:00 Panel discussion on open issues about spin currents and spin Hall effect (Haldane, MacDonald, Niu.....)

15:30 16:00 Raffaele Resta - Kohn's localization and the quantum Hall effect

16:00 16:30 Ivo Souza - Efficient ab initio calculation of the anomalous Hall conductivity by Wannier interpolation

16:30 17:00 Carlo M. Canali - Chern numbers for ferromagnetic metal nanoparticles

WEDNESDAY, JULY 6th

09:00 10:00 Naoto Nagaosa - Disorder effects in Berry phase phenomena

10:00 10:30 Ian Campbell - The anomalous Hall effect in re-entrant AuFe alloys and the real space Berry phase

11:00 11:30 Andrea Dal Corso - Spin-orbit coupling, complex band structures and ballistic conductance with ultrasoft pseudo-potentials

11:30 12:00 Vitalii Dugaev - Anomalous Hall effect in a two-dimensional electron gas with spin-orbit interaction

Presentation Titles & Abstract List

Anomalous Hall effect in a two-dimensional electron gas with spin-orbit interaction

by Vitalii Dugaev, P. Bruno, M. Taillefumier, B. Canals, C. Lacroix

We discuss the mechanism of anomalous Hall effect related to the contribution of electron states below the Fermi surface (induced by the Berry phase in momentum space). Our main calculations are made within a model of two-dimensional electron gas with spin-orbit interaction of the Rashba type, taking into account the scattering from impurities. We demonstrate that such an "intrinsic" mechanism can dominate but there is a competition with the impurity-scattering mechanism, related to the contribution of states in the vicinity of Fermi surface. We also show that the contribution to the Hall conductivity from electron states close to the Fermi surface has the intrinsic properties as well.

Chern numbers for ferromagnetic metal nanoparticles
by Carlo M. Canali

We argue that ferromagnetic transition metal nanoparticles with fewer than approximately 100 atoms can be described by an effective Hamiltonian with a single giant spin degree of freedom. The total spin S of the effective Hamiltonian is specified by a Berry curvature Chern number that characterizes the topologically non-trivial dependence of a nanoparticle's many-electron wavefunction on magnetization orientation. Interestingly, this simple procedure yields the correct Hund's-3rd-rule values for the ground state degeneracies for isolated (open-shell) atoms. The Berry curvatures and associated Chern numbers have a complex dependence on spin-orbit coupling in the nanoparticle and influence the semiclassical Landau-Liftshitz equations that describe magnetization orientation dynamics. Recent work to evaluate effective giant-spin Hamiltonians for realistic transition metal clusters by performing ab-initio calculations of the Berry curvatures will be discussed.

C.M. Canali, A. Cehovin and A.H. MacDonald, Phys.Rev.Lett. 91, 046805 (2003).

Spin-orbit coupling, complex band structures and ballistic conductance with ultrasoft pseudo-potentials
by Andrea Dal Corso

The approach proposed by Choi and Ihm [1] for calculating the ballistic conductance of open quantum systems has been generalized to deal with magnetic transition metals described by ultrasoft pseudo-potentials. [2] I will present some results obtained recently with this method on the spin-resolved conductance of a model Ni nanocontact formed by a three atom monatomic wire placed between two tips made by seminfinite Ni slabs of (001) orientation. [3] Then, I will discuss how this approach can be generalized to treat systems described by spinor wave-functions which allow to describe both non-collinear magnetic structures and systems with spin-orbit coupling. [4] As a first result, I will present the complex band structures of a Pt monatomic wire calculated accounting for spin-orbit effects.

[1] H.J. Choi and J. Ihm, Phys. Rev. B 59, 2267 (1999).

[2] A. Smogunov, A. Dal Corso, and E. Tosatti, Phys. Rev. B 70, 045417 (2004).

[3] A. Smogunov, A. Dal Corso, and E. Tosatti, in preparation.

[4] A. Dal Corso and A. Mosca Conte, Phys. Rev. B 71, 115106 (2005).

Berry Phase Theory of Charge Effects in Insulators
by David Vanderbilt

I will first briefly summarize the Berry-phase theory of electric polarization, which is closely related to the theory of quantized adiabatic charge transport. I will mention some recent topics of interest, including the formulation of a theory of insulators in finite electric field in terms of a coupling of this field to the Berry-phase polarization, and the role of the Berry curvature and metric and the relation of these to each other and to the degree of localization. Returning to the theory of polarization, I will discuss the need for an analogous theory of orbital magnetization, and I will discuss, in general terms, the similarities and differences that may be expected between these two theories.

Kohn localization and the quantum Hall effect
by Raffaele Resta

According to Kohn (1964) theory of the insulating state electron localization, defined in an appropriate sense, is the cause for the insulating behavior in any insulator. Since 1999 onwards, the theory of the insulating state has been reformulated in terms of a localization tensor which provides a measure of electron localization. This tensor is an intensive property, geometric in nature, which characterizes the ground wavefunction (not the individual states): it is finite in any insulator and divergent in any metal. In the special case of noninteracting electrons, the localization tensor of the insulating solid is related to the spherical second moment of the Wannier-function charge distribution. The localization tensor is a ground-state property, related via a fluctuation-dissipation theorem to the system conductivity. So far, the theory has only addressed systems with time-reversal symmetry, in which case the localization tensor is real. I show that in absence of such symmetry the localization tensor is naturally endowed with an imaginary part, proportional to transverse dc conductivity, and quantized in 2d systems. Therefore electron localization can be regarded as the common cause for both vanishing of the dc conductivity and quantization of the transverse one in QH fluids.

W. Kohn, Theory of the insulating state, Phys. Rev. 133, A171 (1964);

R. Resta, Why are insulators insulating and metals conducting?, J. Phys.: Condens. Matter 14, R625 (2002);

R. Resta, Electron localization in the quantum Hall regime, cond-mat/0504054.

Orbital Magnetization in Extended Systems: Numerics and Results
by Timo Thonhauser, Davide Ceresoli, David Vanderbilt, and R. Resta

We present tight-binding calculations of the orbital magnetization in chiral insulators. Our investigations focus on two-dimensional periodic systems with broken time-reversal symmetry and zero Chern number, and on finite samples cut from such systems. Time-reversal symmetry is broken by threading magnetic fluxes through parts of the unit cell in such a way that the net magnetic field remains zero. Results for the calculated magnetization as a function of the flux show that, in the limit of large but finite systems, the orbital magnetization converges to its bulk value as computed in k-space using the formulation presented by Davide Ceresoli. Possible extensions to non-zero Chern numbers and metals will also be discussed.

T. Thonhauser, Davide Ceresoli, David Vanderbilt, and R. Resta, submitted to PRL (cond-mat/0505518).

R. Resta, Davide Ceresoli, T. Thonhauser, and David Vanderbilt, ChemPhysChem, in press (2005).

Efficient ab initio calculation of the anomalous Hall conductivity by Wannier interpolation
by Ivo Souza, Xinjie Wang, Jonathan Yates, and David Vanderbilt

The static intrinsic anomalous Hall conductivity is given by a Brillouin-zone integral of the Berry curvatures of the states below the Fermi surface. It is usually written as a Kubo-formula, which involves a sum over unoccupied states as well. Alternatively, it may be recast in a form where only occupied states appear explicitly. Finally, the non-quantized part can be expressed as a Fermi surface integral[1]. The only ab initio calculations so far[2,3] used the Kubo formula. I will discuss ideas for implementing the other two formulations. The first step is to map the ab initio electronic structure problem onto a tight-binding model, by constructing Wannier functions that accurately describe the ab initio band structure around the Fermi level[4]. The required quantities can then be evaluated very efficiently at arbitrary k points by Wannier interpolation, without having to perform aditional ab initio calculations. That is particularly advantageous for this problem, since an exceedingly fine sampling of certain regions of the Brillouin zone is needed in order to achieve convergence[3].

[1] F. D. M. Haldane, Phys. Rev. Lett. 93, 206602 (2004).

[2] Z. Fang et al,. Science 302, 92 (2003).

[3] Y. Yao et al., Phys. Rev. Lett. 92, 037204 (2004).

[4] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2002).

Orbital Magnetization in Extended Systems: Theory
by Davide Ceresoli , T. Thonhauser, D. Vanderbilt and R. Resta

The magnetic dipole moment of any finite sample is well defined, while it becomes ill defined in the thermodynamic limit, due to the unboundedness of the position operator. The corresponding electrical problem, where surface charges and bulk polarization appear as entangled, has been solved about one decade ago by the modern theory of polarization, based on a Berry phase. We follow a similar path here, providing a bulk expression for orbital magnetization for any lattice-periodical, though time-reversal breaking, Hamiltonian. We therefore limit ourselves to cases where the macroscopic (i.e. cell-averaged) magnetic field vanishes. For crystalline insulators we express the bulk magnetization in terms of Wannier functions, and we then transform the expression into a Brillouin-zone integral involving the occupied Bloch orbitals. Interestingly, the final expression remains well-defined even for metals, but it is not yet clear whether it is correct in that case.

The Quantum Spin Hall Effect
by Charles Kane

We show that the intrinsic spin orbit interaction in a single plane of graphene converts the ideal two dimensional semi metallic groundstate of graphene into a quantum spin Hall (QSH) state [1]. This novel electronic phase shares many similarities with the quantum Hall effect. It has a bulk excitation gap, but supports the transport of spin and charge in gapless "spin filtered" edge states on the sample boundary. We show that the QSH phase is associated with a Z_2 topological invariant, which distinguishes it from an ordinary insulator [2]. The Z_2 classification, which is defined for any time reversal invariant Hamiltonian with a bulk excitation gap, is analogous to the Chern number classification of the quantum Hall effect. We argue that the QSH phase is topologically stable with respect to weak interactions and disorder. The QSH phase exhibits a finite (though not quantized) dissipationless spin Hall conductance even in the presence of weak disorder, providing a new direction for realizing dissipationless spin transport.

1. C.L. Kane and E.J. Mele, cond-mat/0411737
2. C.L. Kane and E.J. Mele, cond-mat/0506581

Spin Hall Effect and Spin Hall Spin Accumulation
by Allan H. MacDonald, Anton Burkov, Tomas Jungwirth, Qian Niu, Kentaro Nomura, Nicolai Sinitsyn, Jairo Sinova

The controlled generation of localized spin-densities is a key enabler of semiconductor spintronics. Finite spin-densities in semiconductors have traditionally been generated by external magnetic fields, by circularly polarized light sources, or by spin injection from ferromagnetic metals. Recently there has been considerable interest in an alternate strategy in which edge spin densities are generated electrically via the spin Hall effect, em i.e. (in a planar device) by the current of spins (j_H^z) oriented perpendicular to the plane that is generated by and flows perpendicular to an electric field. Practical interest in this effect is motivated by arguments that, at least in principle, it may enable low power consumption electronic devices. The spin Hall effect has traditionally been thought of as a consequence of skew-scattering [Dyakonov:1971, Hirsch:1999 ,Kato:2004], spin-dependent chirality in impurity scattering that ocurs in systems with spin-orbit coupling. Recently it has been recognized that the spin Hall effect also has an intrinsic contribution due to spin-orbit coupling in a perfect crystal. I will discuss the various contributions to the spin Hall conductivity and their relationship to the strongly analogous contributions the Hall conductivity of a ferromagnet. One broad classification of contributions is that the spin Hall conductivity is the sum of an interband coherence response contribution that is often dominated by an intrinsic part and a skew scattering contribution. In isotropic two-dimensional electron systems spin-orbit interactions can normally be modelled as momentum dependent Zeeman fields which always point in the plane. In these systems the skew scattering contribution is absent. For a two-dimensional hole gas with strong spin-orbit interactions the spin Hall conductivty is well approximated by its intrinsic contribution. The main observable consequence of the spin Hall effect is the spin accumulations near sample edges to which they give rise. Because spin is not conserved in systems with spin-orbit interactions, there is no unique definition of the spin current. The measure of merit of a particular spin-current definition is its utility for the evaluation of the edge spin accumulations associated with the spin Hall effect. There is not, as yet, a useful and general theory of these spin accumulations in systems with strong spin-orbit interactions. I will present and discuss numerical results which indicate that for a two-dimensional hole gas the edge spin-density is proportional to the spin Hall current and inversely proportional to the hole gas Fermi velocity, and that it is localized within a spin-precession length of the edge.

Disorder effects in Berry phase phenomena
by Naoto Nagaosa

Disorder effects such as the impurity scattering play crucial roles in the transport phenomena and dielectric phenomena governed by the Berry phase curvature. Especially the debates on the intrinsic and extrinsic mechanism of anomalous Hall effect and spin Hall effect still continue with lots of confusions. I will talk on the recent advances on these problems. We found that the magnetic monopole and the associated non-perturbative aspect is essential for the intrinsic mechanism. I will also discuss the role of Anderson localization in anomalous Hall effect and charge pumping.

Pseudopotential Hamiltonian in Magnetic field: the orbital magnetism within a pseudopotential framework
by Francesco Mauri

Anomalous Hall Effect in Ferromagnets
by Patrick BRUNO

Berry Phase Theory of the Anomalous Hall Effect
by F. Duncan M. Haldane

The Karplus-Luttinger formula for the intrisic AHE has been recognized as an integral over the ”Berry Curvature” of all occupied Bloch states. This formula resembles the Landau diamagnetism formula, and appears not to be a Fermi surface formula, in violation of the fundamental principle that all transport processes occur at the Fermi level. Recently I have shown that it is in fact the sum of a quantized part associated with topologically-non-trivial occupied bands, and non-quantized part determined entirely at the (bulk) Fermi surface. There is a simple geometrical formula for the Fermi surface part that is valid in interacting Fermi liquids (like the Luttinger Fermi surface volume theorem, to which it is related); the quantized part is also a Fermi level effect associated with chiral edge states at the Fermi level, which are necessaily present if there are fully-occupied bands with non-trivial topology. These results prompt a new look at ingredients of Fermi liquid theory that were not recognized when that theory was developed. A subtlety about the ”Berry curvature” of Bloch states will also be discussed: it encodes the embedding of Hilbert space in real space in addition to properties of the Bloch wavefunctions.

F. D. M. Haldane, Phys. Rev Lett. 93, 206602 (2004)

Berry phase correction to electron density of states in solids
by Qian Niu

Liouville's theorem on the conservation of phase space volume is violated by Berry phase in the semiclassical dynamics of Bloch electrons. This leads to a modification of the phase space density of states, whose significance is discussed in a number of examples: field modification of the Fermi-sea volume, connection to the anomalous Hall effect, and a general formula for orbital magnetization. The effective quantum mechanics of Bloch electrons is also sketched, where the modified density of states plays an essential role.

On A Proper Definition of Spin Current
by Qian Niu , Ping Zhang, Junren Shi, Di Xiao, Qian Niu

The conventional definition of spin current is incomplete and unphysical in describing spin transport in systems with spin-orbit coupling. A proper and measurable spin current is established in this study, which fits well into the standard framework of near-equilibrium transport theory and has the desirable property to vanish in insulators with localized orbitals. Our theory predicts opposite signs of spin Hall coefficients for a few semiconductor models, urging critical tests of the concept by experiments and numerics.

Ab initio calculation of spin Hall effect in semiconductors and anomalous Hall effect in ferromagnetic insulators
by Guang-Yu Guo , Qian Niu and Yugui Yao

Spin current generation is an important issue in the emerging spintronics technology. Recent proposals of the intrinsic spin Hall effect by Murakami et al [1] and Sinova et al [2], are therefore fascinating. This spin Hall effect would enable spin current generation in semiconductors without magnetic field or magnetic materials, and promise a tremendous potential of combining spintronics with the well-developed semiconductor technology. However, the recent proposals of the intrinsic spin Hall effect have been subject to careful scrutinies. In particular, Wang and Zhang [3] argued that spin symmetry consideration would rule out the possibility of such a spin current in the semiconductors described by the Luttinger Hamiltonian which was used in [1]. On the other hand, Zhang and Yang [4] point out that the intrinsic spin Hall effect predicted in [2], in a two-dimensional electron gas in semicoductors, would be exactly cancelled by the intrinsic orbital-angular-momentum Hall (orbital) effect. Therefore, fundamental questions such as the existence of the intrinsice spin Hall effect in semiconductors structures and that whether it would be cancelled out by the orbital Hall effect, remain unsolved despite enormous recent efforts. In this talk, we report our ab initio relativistic band theoretical calculations on the intrinsic spin Hall effect in the archetypical semiconductors Si, Ge, GaAs and AlAs [5]. Our results cover a large range of hole concentration which is beyond the validity regime of the Luttinger model. We find that intrinsic spin Hall conductivity in hole-doped semiconductors Ge, GaAl and AlAs is large, showing the possibility of spin Hall effect beyond the Luttinger Hamiltonian. The calculated orbital Hall conductivity is one order of magnitude smaller, indicating no cancellation between the spin and orbital Hall effects in bulk semiconductors. Furthermore, it is found that the spin Hall effect can be strongly manipulated by strains, and that the ac spin Hall conductivity in the semiconductors is large in pure and as well as doped semiconductors.

[1] S. Murakami, N. Nagaosa, and S.-C. Zhang, Science 301, 1348 (2003).

[2] J. Sinova et al., Phys. Rev. Lett. 92, 126603 (2004).

[3] X. Wang, and X.-G. Zhang, J. Magn. Magn. Mater. 288, 297 (2005).

[4] S. Zhang, and Z. Yang, Phys. Rev. Lett. 94, 66602 (2005).

[5] G.Y. Guo, Y. Yao, and Q. Niu, Phys. Rev. Lett. 94, 226601 (2005).

Spin Hall Effect
by Tomas Jungwirth , Jairo Sinova

Spin Hall Effect
by Jairo Sinova , Tomas Jungwirth

The anomalous Hall effect in re-entrant AuF alloys and the real space Berry phase
by Ian Campbell, P.Pureur, F. Wolff Fabris, J. Schaf, V.N. Vieira

The Hall effect has been studied in a series of AuFe samples in the re-entrant concentration range, as well as in the spin glass range. The data demonstrate that the degree of canting of the local spins strongly modifies the anomalous Hall effect, in agreement with model predictions associating canting, chirality and the "real space Berry phase". The canonical parametrization of the Hall signal for magnetic conductors becomes inappropriate when local spins are canted.

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4 News from UK's CCP9 Programme

UK's Collaborative Computational Project 9 (CCP9) on "Computational Studies of the Electronic Structure of Solids"

4.1 CCP9 Workshop Announcements

4.1.1 One-day Meeting on Topics in Nanomagnetism

CCLRC Daresbury Laboratory, UK
Wednesday, 30th November, 2005
http://www.cse.clrc.ac.uk/events/Magnetism/

This one-day meeting will take place at CCLRC Daresbury Laboratory on Wednesday 30th November 2005 and will be jointly organised by Prof Walter Temmerman (Daresbury), Dr Werner Hofer (Liverpool), Dr Adrian Wander (Daresbury) and Prof Nic Harrison (Daresbury) on behalf of the CCP3 and CCP9 projects.

The aim of the meeting is to bring together experts from the field of Nano-Magnetism to discuss new developments and future ideas. The meeting will be made up of a series of invited talks given by selected experts from around Europe, and a number of contributed talks given by attendees at the event.

Confirmed speakers include:

Pietro Gambardelli (EPFL Lausanne)
Marco Affronte (INFM National Research Centre)
Balazs Ujfalussy (Hungarian Academy of Science)
Amadeo Vazquez de Parga (Universidad Autonoma de Madrid)
John Jefferson (QinetiQ)

Further information and details of how to register can be found at

http://www.cse.clrc.ac.uk/events/Magnetism/

5 News from the NANOQUANTA Network

5.1 Reports on Workshops of the NANOQUANTA Network

5.1.1 Report on the 356th Wilhelm and Else Heraeus Seminar "40 Years of the *GW* Approximation for the Electronic Self-Energy: Achievements and Challenges"

Physikzentrum Bad Honnef, Germany

12–15 September 2005

Sponsors:
Wilhelm and Else Heraeus Foundation
NANOQUANTA Network of Excellence

Organisers:
Arno Schindlmayr (Forschungszentrum Jülich, Germany)
Pablo García-González (UNED, Madrid, Spain)
Maurizia Palummo (Università di Roma "Tor Vergata", Italy)
Olivia Pulci (Università di Roma "Tor Vergata", Italy)
Nathalie Vast (Ecole Polytechnique, Palaiseau, France)

http://www.fz-juelich.de/iff/GW2005

The *GW* approximation has become an indispensable tool for ab initio electronic-structure calculations, because it allows an accurate quantitative determination of excited states in solids that cannot be matched by variational ground-state schemes like static density-functional theory or quantum Monte Carlo. It is therefore regarded as a reference method against which other computational schemes must be judged. Although the *GW* approximation itself is only applicable to single-particle spectra, generalisations like the Bethe-Salpeter equation have also been successfully used to study optical properties and collective excitations, such as excitons in semiconductors. In addition, increasingly powerful computing facilities have now made it possible to study complex nanostructured materials, opening exciting perspectives for applications in nanoscience.

Building on earlier Green-function techniques, the *GW* approximation was introduced by Lars Hedin in 1965 and initially applied to the homogeneous electron gas. The accurate prediction of the quasiparticle band structure immediately sparked a series of papers examining other aspects of the single-particle spectrum, indicating the potential power of this new approach. However, it took twenty years until numerical calculations for real solids became feasible in 1985, when first-principles band gaps for silicon and diamond were reported in excellent agreement with experiments. Since then the *GW* approximation has flourished: besides band structures, it has been used to obtain quasiparticle lifetimes, photoemission spectra and even total energies for a wide range of materials. Other studies have illuminated the theoretical foundations and led to further extensions, for instance into the strongly correlated regime. Now, another twenty years later, it was time to assess the present achievements and examine the perspectives for future developments. In particular, the topics of this seminar included basic problems like the interrelation of self-consistency and vertex corrections, novel applications to complex materials, the relation to other electronic-structure methods as well as computational implementation strategies.

In the opening talk of the seminar, Carl-Olof Almbladh recounted the circumstances under which Lars Hedin developed the *GW* approximation, stressing his intention to obtain a manageable and reliable scheme for interacting electrons in solids at a time when most published results on many-body theory were of a purely formal nature. Rodolfo Del Sole and Lucia Reining continued this historical overview by highlighting milestones in the application of the *GW* approximation to real materials, which started in the 1980s, and more recent calculations of optical spectra based on the Bethe-Salpeter equation. The other sessions on the first day gave an impression of the variety of systems that can now be treated within the *GW* approximation, such as high-k dielectrics, defects or systems with localised d and even f electrons. Although usually seen as a method for periodic solids, several talks demonstrated that the *GW* approximation can also yield good results for finite systems, ranging from small nanoclusters to fullerenes and large organic molecules. Increasingly, computer codes are already developed specifically for such applications as an alternative to more expensive quantum-chemical approaches. For example, Wolfgang Hübner presented an implementation without periodic boundary conditions, based on Gaussian-type basis functions, and Thomas Niehaus reported a tight-binding implementation that allows investigations of large molecules.

The second day of the seminar was mostly concerned with the calculation of optical spectra from the Bethe-Salpeter equation, whose practical solution is typically based on the time-dependent *GW* approximation, i.e., the summation of ladder diagrams with the screened Coulomb interaction. Friedhelm Bechstedt and others demonstrated that this field is now mature enough to produce accurate spectra not only for bulk materials but also for complex surfaces and nanostructures. As a noteworthy example for direct impact on experimental investigations, Wojciech Wełnic explained how calculations of optical spectra for different geometries of GeTe helped to track modifications of the local atomic order of this phase-change material upon amorphisation. Going beyond a treatment of the electron system alone, Steven Louie showed how forces can be derived from the gradient of the excited-state energy surface with respect to the atomic coordinates, leading to local lattice distortions and self-trapped excitons, for instance in SiO_2. Another aspect of time evolution was presented by Michael Rohlfing, who discussed the dynamics of resonant charge transfer from an electronically excited adsorbate to a substrate surface, illustrated by the system CO:MgO(001)-(1×1). Finally, leading over to the focus of the third day, Christoph Friedrich reexamined a controversy that had dominated excited-state meetings in recent years, namely the apparent discrepancy between pseudopotential and all-electron *GW* results. Careful calculations for Si as a prototype material showed that better convergence with respect to the number of unoccupied states and the removal of (numerically small) linearisation errors in LAPW and LMTO implementations partially remove the discrepancy, which, though not fully resolved, is eventually comparable to the usual spread between different codes.

The third day started with a session on time-dependent density-functional theory, in which Angel Rubio highlighted the fruitful connections with many-body perturbation theory, which has, on the one hand, enabled efficient calculations within the density-functional formalism for complex systems, such as surfaces or biomolecules, and on the other hand, led to accurate exchange-correlation kernels derived by many-body methods. This was subsequently illustrated by many applications, for example the optical absorption spectra of DNA bases presented by Daniele Varsano. The central topic of the third day, however, was the examination of different ways of going beyond the standard *GW* approach, which is based on first-order perturbation theory starting from the Kohn-Sham eigenvalue spectrum and is thus often negatively affected by the poor performance of the local-density approximation in the underlying density-functional calculation, especially in systems involving transition-metal elements or semi-core states. As fully self-consistent *GW* approaches were previously shown to destroy spectral features, Takao Kotani proposed a novel restricted algorithm in which only the quasiparticle excitations are iterated to self-consistency. Results for a large number of different materials showed consistently good agreement with experimental data. Diagrammatic vertex corrections beyond the *GW* approximation were discussed by Ulf von Barth and Luca Molinari, but applications to complex systems are ruled out by the rapidly increasing computational expense. As an alternative, Ferdi Aryasetiawan presented a successful combination of the *GW* self-energy for long-range correlation with the nonperturbative dynamical mean-field theory, which describes short-range correlation more accurately and is even capable of treating Mott-Hubbard insulators, which are out of reach of many conventional ab initio techniques.

The last day of the seminar further examined electronic-structure calculations for transition metals and also compared the *GW* approximation to alternative approaches like self-interaction corrections within density-functional theory. Of particular interest was the *GW* implementation within the multiple-scattering KKR method presented by Arthur Ernst: although computationally involved, this technique allows the treatment of nonperiodic systems like surfaces or defects without artificial supercells, which invariably lead to finite-size errors in traditional calculations. In the final session, Xavier Gonze discussed how the experience from many-body perturbation theory can be exploited to construct orbital-dependent functionals for density-functional theory, and Nuno Carneiro exploited the electronic self-energy to derive a novel generalised Kohn-Sham scheme for efficient total-energy calculations.

Besides the oral presentations, the seminar programme contained a poster session, which, in particular, many younger participants used to discuss their work with colleagues from other institutes. The lively discussions and exchange of ideas were furthered by the inspiring atmosphere of the Physikzentrum Bad Honnef, which offered not only state-of-the-art technical equipment but also full-board accommodation on site, including the downstairs “Bürgerstube” for informal gatherings in the evenings. The financial support of the Wilhelm and Else Heraeus Foundation, which funded the invited speakers and in addition provided most young researchers with bursaries covering all local costs, is gratefully acknowledged.

This seminar was part of an annual workshop series on electronic excitations organised by members of the European Network of Excellence NANOQUANTA. Previous meetings in this series focused on *Ab initio Theoretical Approaches to the Electronic Structure and Optical Spectra of Materials* (Lyon, 2002), *Ab initio Electrons Excitations Theory: Towards Systems of Biological Interest* (San Sebastian, 2003) and *Theory and Modeling of Electronic Excitations in Nanoscience* (Acquafredda di Maratea, 2004). The series will continue with a workshop in Louvain-la-Neuve in September 2006.

Programme

Sunday, 11 September 2005

Arrival and registration

18:00–21:00 Registration

18:30 Buffet dinner

Monday, 12 September 2005

8:00 Breakfast

9:00– 9:20 Arno Schindlmayr (Forschungszentrum Jülich, Germany)
Welcome

Development of the *GW* approximation

9:20– 9:40	Carl-Olof Almbladh (Lunds Universitet, Sweden) *Lars Hedin and the GW approximation—the first 20 years*
9:40–10:20	Rodolfo Del Sole (Università di Roma “Tor Vergata”, Italy) *Twenty years of GW in Rome*
10:20–10:40	Lucia Reining (Ecole Polytechnique, Palaiseau, France) *Theoretical spectroscopy: Some developments and applications based on GW*
10:40–11:10	Coffee break

Quasiparticle calculations for solids

11:10–11:50	Patrick Rinke (Fritz-Haber-Institut, Berlin, Germany) *Excited states in semiconductors and insulators: Ab inito quasiparticle band structures of II-VI compounds, group-III nitrides and high-k dielectrics*
11:50–12:10	Hung Chung Hsueh (Tamkang University, Tamsui, Taiwan) *Quasiparticle excitations of native defects in III-V semiconductors: GW approximation*
12:10–12:50	Andrzej Fleszar (Universität Würzburg, Germany) *GW calculations for compounds with d and f electrons*
13:00	Lunch

Quasiparticle calculations for finite systems

14:20–15:00	Wolfgang Hübner (Technische Universität Kaiserslautern, Germany) *GW calculations on Na and Pt clusters*
15:00–15:20	Eleonora Luppi (Università di Modena e Reggio Emilia, Italy) *Emission properties of small hydrogenated and oxidised silicon nanoclusters*
15:20–15:40	Emanuela Pusceddu (Università degli Studi di Cagliari, Italy) *Quasiparticle energies and optical properties of small fullerenes*
15:40–16:00	Thomas Niehaus (Universität Paderborn, Germany) *Quasiparticle energies for large molecules: A tight-binding GW approach*
16:00–16:30	Coffee break

Poster session

16:30–18:30	Poster session The posters remain on display throughout the seminar
18:30	Dinner Followed by a social evening at the invitation of the Wilhelm and Else Heraeus Foundation in the “Bürgerstube” at the Physikzentrum

Tuesday, 13 September 2005

8:00	Breakfast

Many-body effects in spectroscopy

9:00– 9:40	Eberhard K. U. Gross (Freie Universität Berlin, Germany) *The fundamental gap in reduced-density-matrix-functional theory*
9:40–10:00	Lucia Caramello (Universit degli Studi di Milano, Italy) *A Hilbert-transform-based scheme for efficient computation of response functions and its application to study the optical properties of the oxidised Si(100)-(2×2) surface*
10:00–10:20	Luis Ramos (Universität Jena, Germany) *Electronic and optical properties of Si and Ge nanocrystallites: Influence of oxidation, capping and doping*
10:20–10:40	Aleksi Soininen (University of Helsinki, Finland) *Quasiparticle effects in inelastic X-ray scattering*
10:40–11:10	Coffee break

Exciton dynamics

11:10–11:50	Steven G. Louie (University of California at Berkeley, USA) *Ab initio study of the photo-excited state: Nanotubes to self-trapped excitons*
11:50–12:10	Mauro Bruno (Università di Roma "Tor Vergata", Italy) *Excitons in germanium nanowires: Quantum confinement, orientation and anisotropy effects*
12:10–12:50	Michael Rohlfing (International University Bremen, Germany) *Time dynamics of electron-hole excitations*
13:00	Lunch

Electronic properties of nanostructured materials

14:20–15:00	Friedhelm Bechstedt (Universität Jena, Germany) *GW approximation for electronic excitations beyond standard treatment*
15:00–15:20	Christoph Friedrich (Forschungszentrum Jülich, Germany) *Converged all-electron GW approximation in the augmented-plane-wave basis-set limit*
15:20–15:40	Wojciech Wełnic (Ecole Polytechnique, Palaiseau, France) *Local atomic order and optical properties in amorphous and laser-crystallised GeTe with ab initio methods*
15:40–16:00	Igor Campillo (Labein Centro Tecnológico, Derio, Spain) *Silicate chain formation in the nanostructure of cement-based materials*
16:00–16:30	Coffee break

NANOQUANTA general network meeting

16:30–18:30	NANOQUANTA general network meeting
18:30	Dinner

Wednesday, 14 September 2005

8:00	Breakfast

Time-dependent density-functional theory

9:00– 9:40	Angel Rubio (DIPC, San Sebastian, Spain) *A TDDFT-based formalism for the response of solids, nanostructures and biomolecules*
9:40–10:00	Daniele Varsano (DIPC, San Sebastian, Spain) *A TDDFT study of excited states of DNA bases and base assemblies*
10:00–10:20	Gianluca Stefanucci (Lunds Universitet, Sweden) *An ab initio theory of transport using TDDFT and nonequilibrium Green functions*
10:20–10:40	Viviana Garbuio (Università di Roma “Tor Vergata”, Italy) *Ab initio study of the excited-state properties of liquid water*
10:40–11:10	Coffee break

Beyond the *GW* approximation (1)

11:10–11:50	Rex W. Godby (University of York, United Kingdom) *GW and beyond*
11:50–12:10	Adrian Stan (Rijksuniversiteit Groningen, The Netherlands) *Fully self-consistent GW calculations for atoms and molecules*
12:10–12:50	Ulf von Barth (Lunds Universitet, Sweden) *Vertex corrections to the GW approximation*
13:00	Lunch

Beyond the *GW* approximation (2)

14:20–15:00	Takao Kotani (Arizona State University, Tempe, USA) *Quasiparticle self-consistent GW method*
15:00–15:20	Fabien Bruneval (Ecole Polytechnique, Palaiseau, France) *Electronic structure of Cu_2O within self-consistent GW*
15:20–16:00	Ferdi Aryasetiawan (AIST, Tsukuba, Japan) *Merging first-principles and model approaches: GW+DMFT*
16:00–16:30	Coffee break

Many-body perturbation theory and metallic systems

16:30–17:10	Luca Molinari (Università degli Studi di Milano, Italy) *Hedin’s equations and enumeration of Feynman diagrams*
17:10–17:30	Paul Ziesche (MPI für Physik komplexer Systeme, Dresden, Germany) *The high-density electron gas and the peculiarities of its reduced densities, its self-energy and the Hugenholtz–van Hove identity*
17:30–17:50	Nicola Manini (Università degli Studi di Milano, Italy) *Many-body properties of a jellium slab*
17:50–18:10	Maia García-Vergniory (Euskal Herriko Unibertsitatea, Bilbao, Spain) *Lifetimes of Shockley electrons and holes at the Cu(111) surface*
18:10–18:30	Andrea Ferretti (Università di Modena e Reggio Emilia, Italy) *First-principles description of transport including electronic correlation*
18:30	Dinner

Thursday, 15 September 2005

8:00	Breakfast

Electronic-structure methods for transition metals

9:00– 9:40	Arthur Ernst (MPI für Mikrostrukturphysik, Halle, Germany) *GW approximation for correlated systems within the multiple-scattering method*
9:40–10:00	Uwe Birkenheuer (MPI für Physik komplexer Systeme, Dresden, Germany) *Wave-function-based determination of the quasiparticle band structure of solids and polymers*
10:00–10:20	Chaitanya Das Pemmaraju (Trinity College, Dublin, Ireland) *Investigation using the pseudopotential SIC-LSDA into the role of n-type defects in DMS ZnO:Co*
10:20–10:40	Virginie Trinité (Ecole Polytechnique, Palaiseau, France) *Self-interaction-corrected (SIC) pseudopotential for Ti and* TiO_2
10:40–11:10	Coffee break

Developments in density-functional theory

11:10–11:50	Xavier Gonze (Université Catholique de Louvain, Belgium) *Orbital- and energy-dependent exchange-correlation functionals*
11:50–12:10	Nuno Carneiro (University of York, United Kingdom) *A novel generalised Kohn-Sham scheme*
12:10–12:30	Andrea Floris (Freie Universität Berlin, Germany) *Density-functional theory for superconductors: Applications to* MgB_2*, Pb and solids under pressure*
12:30–12:50	Arno Schindlmayr (Forschungszentrum Jülich, Germany) Farewell
13:00	Lunch

Abstracts of Lectures

Lars Hedin and the *GW* approximation—the first 20 years

Carl-Olof Almbladh
Solid State Theory, Physics Department, Lund University, Lund, Sweden

The early sixties was a very exciting period in the development of many-body theory as applied to solids. In this talk I will concentrate on the development in the group of Stig Lundqvist, Lars Hedin and Bengt Lundqvist, and the importance of their work for future applications. In particular, the development of the *GW* theory will be discussed.

Twenty years of *GW* in Rome

Rodolfo Del Sole
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The microscopic study of complex systems has nowadays reached a high level of accuracy that allows for a deep understanding of the electronic excitations. Ab initio descriptions of experiments such as direct or inverse photoemission, optical absorption, electron energy loss, have become possible thanks to the huge progress in theory and increased computational power. Charged excitations, as well as neutral excitations, can now be studied within the many-body perturbation theory based on the Green's function formalism. Optical spectra can be calculated with inclusion of the electron-hole interaction by solving the Bethe-Salpeter equation (BSE) within the framework of Green's function theory. This has been made possible by the seminal work of Lars Hedin in 1965, who derived a set of equations (Hedin's equations) to describe excited states. Moreover, optical spectra can also nowadays be well described within the time-dependent density-functional theory (TDDFT).

In this seminar I will review some of the work carried out on these topics in Rome since 1985, when a collaboration with Friedhelm Bechstedt started with the purpose of finding a recipe for a fast, simplified, yet accurate, *GW* method. I will also describe the most recent results, i.e., for the electronic structure and optical properties of diamond and silicon surfaces within the DFT, *GW* and BSE approaches. A test of the TDDFT approach to the optical properties will be shown for the case of Si(111)-(2×1).

Theoretical spectroscopy: Some developments and applications based on *GW*

Lucia Reining
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In this talk, I will give a very brief overview of some work done in our group in Palaiseau, often in collaboration, during the last 10 years. I will focus on subjects for which we were essentially using Lars Hedin's *GW* approximation or starting from it for further developments. The topics in this list range from clusters to bulk materials, from approximate *GW* calculations and technical developments to vertex corrections beyond the random-phase approximation and beyond *GW*.

Excited states in semiconductors and insulators: Ab inito quasiparticle band structures of II-VI compounds, group-III nitrides and high-*k* dielectrics

Patrick Rinke
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Photo-electron spectroscopy has developed into an invaluable experimental tool for the study of electron excitations in bulk solids and surfaces. The success of photoemission spectroscopy (PES) and its inverse counterpart (IPES) owes much to the interpretation of the photo-electron spectra in terms of single-particle excitations or quasiparticles in the language of many-body quantum mechanics. For solids Hedin's *GW* approximation, where *G* refers to the Green's function and *W* to the dynamically screened Coulomb interaction, has become the method of choice for an ab initio calculation of the quasiparticle energy spectrum. The *GW* method is applied to different crystalline phases of HfO_2, which has received considerable interest as an alternative gate material (high-*k*) in complementary metal-oxide semiconductor (CMOS) transistors, to shed light on the structural dependence of the excitation spectrum. For describing systems with semicore electrons like II-VI compounds and group-III nitrides, which are important for the optical industry, a new, alternative approach based on combining *GW* with density-functional theory (DFT) in the exact-exchange formalism (OEPx) will be presented [1].

[1] P. Rinke et al., New J. Phys. **7**, 126 (2005).

Quasiparticle excitations of native defects in III-V semiconductors: *GW* approximation

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The III-V systems have received much attention due to their technological applications. Especially, the group-III nitrides form an important class in the major semiconductors that are currently under development for devices requiring wide band gaps. As in all semiconductors, understanding the effects of native defects is required to implementation of devices made from these materials. In this work, we study the structural and electronic properties of various point defects (vacancies and antisites) in III-V semiconductors by ab initio calculations using the pseudopotential plane-wave approach. To model an isolated native defect, a supercell technique was used. Using the spin-polarized *GW* approximation, we examined the electronic structure of defects to provide accurate estimates of defect-induced levels. The calculated equilibrium atomic configurations of vacancies and antisites obtained within density-functional theory (DFT) show Jahn-Teller-like distortions. Calculated energetic locations of defect levels can be compared with available measurements and explain the nature and the origin of the experimental data.

GW calculations for compounds with *d* and *f* electrons

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Strong correlations are in most cases due to the presence of *d* or *f* electrons. Traditionally, however, the *GW* approach has been applied with the biggest success to *sp* systems. In my talk I will present results of *GW* calculations for systems with *d* and *f* electrons. These test cases are: (i) II-VI compounds, where the shallow but fully occupied *d*-electron shell places this class of materials at the border between weakly and strongly correlated systems, (ii) the 3*d* compound MnTe and (iii) the 4*f* compound PrO_2.

GW calculations on Na and Pt clusters

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Quantum-chemical ab initio methods such as configuration interaction (CI) and coupled-cluster (CC) approaches accurately predict ground- and excited-state properties of systems without translational invariance and target optical absorption experiments. Green-function methods, on the other hand, yield the state-specific lifetimes of quasiparticles and collective excitations, properties that are very hard to obtain by any correlated quantum-chemical method. Thus, a Green-function approach is a theoretical counterpart of the rapidly developing time-resolved electron spectroscopies, such as 2-photon photoemission (TR-2PPE).

We present an implementation of the *GW* approximation for the calculation of electronic properties of clusters or molecules such as Na_n^+ ($n < 25$) and Pt_3 without periodic boundary conditions. We expand all quantities in Gaussian-type basis functions, an approach widely used in quantum chemistry, and compute the Green function, screened interaction and self-energy on the real axis of the frequency domain. The dielectric function $\epsilon(\omega)$ is treated without previously employed simplifications, such as the plasmon-pole approximation. Convolutions are performed using fast Fourier transforms to the real time and back. As a test example we use in particular the widely studied Na_9^+ cluster where our self-consistent *GW* calculations indicate convergence of relevant quantities (band gap, screened interaction, self-energy and Green function) already after four cycles. Self-consistency reduces the band gap from values of 4.5 eV (Hartree-Fock) and 3.7 eV (non-self-consistent *GW*) to 3.38 eV. Besides, the plasmon peak narrows due to renormalisation of the broadening of the quasiparticle states. Its half-maximum width corresponds to a plasmon lifetime of approximately 4.1 fs in agreement with experiments on similar systems. In order to study substrate effects on lifetimes we also employ quantum chemistry for the system Na_9^+/Cu(100), where the surface is modelled by an arrangement of 54 Cu atoms. We find a shift and broadening of the collective excitation as the cluster-surface separation shrinks. This ab initio result is analysed further by a combination of image-charge and Mie theory.

Emission properties of small hydrogenated and oxidised silicon nanoclusters

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Silicon nanocrystals (Si-Nc) are promising as silicon-based light-emitting materials. Recent experimental data have demonstrated that surface chemistry produces substantial impact on the optoelectronic properties of Si-Nc. We have investigated the optical response of Si-Nc with different surface termination using ab initio techniques within the DFT. The absorption and emission energies have been calculated within the ΔSCF approach taking into account the structural rearrangement of the atoms within the cluster geometry both in the ground and excited state. This explains the difference between absorption and emission values, i.e., the Stokes shift. For the calculation of the optical spectra we have used different levels of approximation: RPA with and without the inclusion of the local field, quasiparticle corrections within the GW approximation, electron-hole interaction within the BSE and TDDFT approach. These calculations have been performed for both the structural geometry of ground and excited state. In particular we have focused our attention on the Si_{10}-Nc considering the fully hydrogen-terminated cluster ($Si_{10}H_{16}$) and the cluster with oxygen ($Si_{10}H_{14}O$) with two different types of oxygen bonds at the surface: Si=O double bond and Si-O-Si bridge bond. For all these systems the GW shift is quite big and there is a substantial cancellation between self-energy and electron-hole interaction effects. In each structure the optical spectra show at the energy onset a smooth increase of their behaviour, with a single important exception in the emission spectra of the oxidised cluster with O in the bridge. Here a very intense excitonic peak is present. The Stokes shift calculated within the ΔSCF, BSE and TDDFT are quite similar, again the only difference is for the system with the oxygen atom in the bridge configuration.

Quasiparticle energies and optical properties of small fullerenes

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We present theoretical results on the electronic excitations and optical properties of small fullerenes, namely C_{24}, C_{28}, C_{32} and C_{36}. Quasiparticle-corrected HOMO-LUMO gaps have been computed through the ΔSCF scheme. Photoabsorption spectra have been obtained in the framework of time-dependent density-functional theory. Calibration calculations performed for C_{20} and C_{60} result in good agreement with the available experimental and theoretical data.

Quasiparticle energies for large molecules: A tight-binding *GW* approach

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[3]*National Nanotechnology Laboratories of INFM, Università di Lecce, Distretto Tecnologico, Via Arnesano, 73100 Lecce, Italy*
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We present a tight-binding-based *GW* approach for the calculation of quasiparticle energy levels in confined systems such as molecules. Key quantities in the *GW* formalism like the microscopic dielectric function or the screened Coulomb interaction are expressed in a minimal basis of spherically averaged atomic orbitals. All necessary integrals are either precalculated or approximated without resorting to empirical data. The method is validated against first-principles results for benzene and anthracene, where good agreement is found for levels close to the frontier orbitals. Further, the size dependence of the quasiparticle gap is studied for conformers of the polyacenes ($C_{4n+2}H_{2n+4}$) up to $n = 30$.

The fundamental gap in reduced-density-matrix-functional theory

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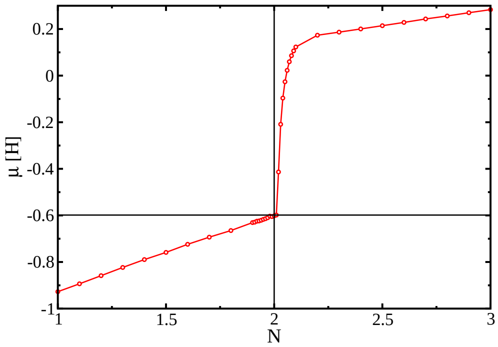
We propose a novel method for calculating the fundamental gap, Δ. This quantity is defined as the difference between the ionisation potential and the electron affinity. Given a system with integer particle number N_0, the fundamental gap can be expressed rigorously as the discontinuity which the chemical potential $\mu(N)$ exhibits at the integer N_0, i.e., $\Delta = \mu(N_0 + \eta) - (N_0 - \eta)$, with a positive infinitesimal η. In the context of density-functional theory this formula leads to the famous representation of the gap as $\Delta = \delta\epsilon + \Delta_{\text{xc}}$, where $\delta\epsilon$ is the energy difference between the lowest unoccupied and the highest occupied Kohn-Sham orbital, and Δ_{xc} amounts to the discontinuity of the exchange-correlation potential upon adding and substracting a fractional charge with respect to the N_0-electron system. Here we investigate the discontinuity of the chemical potential in the context of reduced-density-matrix-functional theory (RDMFT). Employing well-known reduced-density-matrix functionals [1] for the exchange-correlation energy we minimise the total energy with the appropiate constraints ensuring N-representability of the density matrix and conservation of the total particle number. We demonstrate [2] that the resulting discontinuity of the chemical potential represents an excellent measure of the gap, far superior to LDA or GGA calculations. The figure below shows the calculated chemical potential $\mu(N)$ for the H_2 molecule.



Furthermore, we generalise RDMFT to treat open-shell systems by introducing spin-dependent occupation numbers for spin-independent natural orbitals [3]. We demonstrate that the additional constraint of total-spin conservation is indispensible for the proper treatment of open-shell systems: It reduces the difference between calculated and experimental total energies by a factor of 2.

[1] A. M. K. Müller, Phys. Lett. A **105**, 446 (1984).
[2] N. Helbig, N. N. Lathiotakis, M. Albrecht and E. K. U. Gross, cond-mat/0504436.
[3] N. N. Lathiotakis, N. Helbig and E. K. U. Gross, cond-mat/0504435.

A Hilbert-transform-based scheme for efficient computation of response functions and its application to study the optical properties of the oxidised Si(100)-(2×2) surface

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We have formulated an efficient scheme to evaluate the independent-particle dynamic polarisation $\chi^0(\omega)$, used as a starting point in TDDFT to calculate the optical response of a system. The new method has been implemented in the DP ab initio code, improving its time scaling. We demonstrate that this new method is convenient to evaluate the dielectric function of large systems (hundreds of atoms in the unit cell). We applied this method to study the dielectric function of the oxidised Si(100)-(2×2) surface including for the first time the local-field effect in calculating the polarisability and the reflection anisotropy spectra (RAS and SDR).

Electronic and optical properties of Si and Ge nanocrystallites: Influence of oxidation, capping and doping

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Si nanocrystallites (NCs) are interesting structures from the technological point of view, since one can exploit their quantum-confinement properties in electronic devices. For instance, the confinement of carriers in the same region of space can enhance radiative recombination and make nanostructures of indirect-gap materials like Si emit light. Although in recent years, progress has been achieved to understand the luminescence from Si nanostructures, their application in devices, such as lasers, is not yet a reality. In an attempt to obtain optical gain in Si NCs, many factors that influence the light emission have been identified. Besides the size of the NCs, which determines mainly the quantum-confinement effects, oxidation and the presence of defects are some of the factors that can affect the efficiency of optical transitions in Si NCs. Si nanocrystalline samples usually correspond to an ensemble of Si NCs that makes difficult the interpretation of the physical phenomena involved in light emission. In this sense, theoretical models accounting for isolated NCs are useful to individualise the properties of those particles. By applying an ab initio pseudopotential method, we present an investigation of free-standing Si and Ge NCs, concerning their size, passivation, Si oxidation, capping and doping [1]. The main chemical trends for the electronic and optical properties of NCs can be obtained by means of the ground-state treatment provided by density-functional theory, the local-density and generalised gradient approximations. However, to account partially for excitations we also employ the Δ self-consistent-field method, *GW* method, and we solve the Bethe-Salpeter equation to calculate electronic structure and optical absorption spectra. Using those methods, certain aspects of passivation, oxidation, capping, single terminations and substitutional impurities in Si and Ge NCs can be understood [1].

[1] L. E. Ramos, F. Furthmüller and F. Bechstedt, Phys. Rev. B **70**, 033311 (2004); **71**, 035328 (2005); **72** (in press).

Quasiparticle effects in inelastic X-ray scattering

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We will present computational results for nonresonant inelastic X-ray scattering (NRIXS) from core electrons in solids. The behavior of the core excited states is dominated by the localisation of the core hole. In practice this means that the problem can be written as an effective single-particle problem for the final-state electron. The effect of the core hole–electron interaction, the final-state electron quasiparticle shifts and the final-state electron lifetime are clearly visible in the spectra.

We apply a band-structure-based approach [1] to the analysis of NRIXS from core-excited states. The role of the electron-hole interaction will be reviewed. We use a simple G_0W_0 approach [2,3] to approximate the quasiparticle effects. Comparison of the calculated spectra with experimental ones clearly shows that accurate quasiparticle corrections are needed for quantitative analysis. The results highlight the capabilities and some limitations of the current GW-based scheme. Analysis of the final-state local density of states with respect to the momentum-transfer dependence of NRIXS cross sections will also be discussed.

[1] J. A. Soininen and E. L. Shirley, Phys. Rev. B **64**, 165112 (2001).
[2] J. A. Soininen, E. L. Shirley and J. J. Rehr, J. Phys.: Condens. Matter **15**, 2573 (2003).
[3] J. A. Soininen, J. J. Rehr and E. L. Shirley, Physica Scripta T **115**, 243 (2005).

Ab initio study of the photo-excited state: Nanotubes to self-trapped excitons

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We discuss some recent progress on first-principles study of excited-state properties, in particular the optical response of condensed-matter systems. As examples, we present results on the optical properties of nanotubes and on the phenomenon of self-trapped excitons in SiO_2. The approach involves solving for the quasiparticle and electron-hole excitations of the interacting electron system within the GW approximation. In the study of self-trapped excitons, calculation of forces on the atoms in the excited state is further required. Owing to their reduced dimensionality, many-electron effects qualitatively alter the optical spectra of the nanotubes. It is discovered that exciton states in the semiconducting carbon nanotubes have binding energies that are orders of magnitude larger than bulk semiconductors and hence they dominate the optical spectrum at all temperature, and that bound excitons can exist even in metallic carbon nanotubes. Similar studies show that excitonic effects are even stronger in the BN nanotubes. In SiO_2, the excited electron and hole spontaneously distort the crystal, and the exciton self-traps locally to the distortion (to a lower-energy configuration in the excited state) leading to a huge Stokes shift of over 6 eV in the photoluminescence frequency. The calculations provide a microscopic picture of the trapping mechanism and geometry of the self-trapped exciton. The physics behind these phenomena is discussed.

Excitons in germanium nanowires: Quantum confinement, orientation and anisotropy effects

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Within a first-principles DFT framework we show how many-body effects crucially modify the electronic and optical properties of free-standing germanium nanowires. A clear dependence of the excitonic binding energy and localisation length, not only from the wire size, but also from the wire orientation has been found. Moreover, in some of the analysed quantum wires we observe an almost complete compensation of the self-energy and excitonic effects, explaining it in terms of their geometrical atomic structure.

Time dynamics of electron-hole excitations

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We address the time dynamics of excited electronic states, in particular of correlated electron-hole excitations, within ab initio many-body perturbation theory. The excited states are described within the *GW* approach (for electrons and holes) and within the Bethe-Salpeter equation (BSE) for coupled electron-hole pair excitations. In this talk we focus on the resulting time dynamics of the electronic and geometric degrees of freedom. As an example for electronic femtosecond dynamics of excited states we discuss resonant charge-transfer processes from electronically excited adsorbates to a substrate surface, in particular in the system CO:MgO(001)-(1×1). Picosecond dynamics of the atomic structure, as resulting from electronic excitation, can lead to structural relaxation or to dissociation of a system. As examples, we investigate excited-state relaxation of PPP, as well as atom expulsion from alkali halide surfaces.

Work done in collaboration with N.-P. Wang, P. Krüger, J. Pollmann, E. Artacho, M. Côté, P. D. Haynes, R. J. Needs and C. Molteni.

GW approximation for electronic excitations beyond standard treatment

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We demonstrate the power of many-body perturbation theory in the *GW* approximation to describe single-particle and pair excitations in complex systems. The method is based on solutions of the Dyson and Bethe-Salpeter equations and the dynamically screened Coulomb interaction. Together with the supercell approach it can be applied to complex systems, e.g. molecules on surfaces, which involve both extended and localised states. On the single-particle level we discuss effects beyond G_0W_0, pure electronic screening and first-order perturbation theory. A possible approach is presented to treat systems with a wrong energetical ordering of the Kohn-Sham states. It is shown that an initial-state formulation of the time-dependent optical polarizability allows computations of optical spectra for systems with many atoms in the unit cell. The effect of dynamical screening and $\delta W/\delta G$ contributions to the interaction kernel is studied on the two-particle level. Applications of the *GW* approximation to single-particle and pair excitations are presented for three classes of materials: molecules (silan, water), surfaces (hydrogenated Si surfaces) and polar crystals (InN, ice, NaCl).

Converged all-electron *GW* approximation in the augmented-plane-wave basis-set limit

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The *GW* approximation for the electronic self-energy is known to yield quasiparticle band structures in much better agreement with experimental measurements than the local-density approximation (LDA) for a large class of materials. However, almost all actual implementations so far are based on the plane-wave pseudopotential approach, which effectively restricts applications to simple metals and *sp*-bonded semiconductors. In order to overcome this limitation, we have developed an alternative implementation within the all-electron full-potential linearised augmented plane-wave (FLAPW) method, which is also applicable to systems with localised electrons like transition metals or rare-earth elements. Additional simplifications, such as plasmon-pole models, are avoided. While the FLAPW method treats the core electrons explicitly and does not suffer from the uncontrolled pseudisation of the wave functions, another source of errors resulting from the linearisation is frequently overlooked. This arises because the radial wave functions in the muffin-tin spheres are expanded around fixed reference energies. Irrelevant for the valence bands in density-functional theory, it cannot be ignored in the *GW* approximation, where unoccupied states more than 100 eV above the Fermi level must typically be included in the self-energy to guarantee converged results. To eliminate this error, we have improved the FLAPW basis set by including second and higher energy derivatives of solutions to the radial scalar-relativistic Dirac equation in the form of local orbitals. With this modification, we show that the eigenstates converge systematically towards the exact APW spectrum, which contains no linearisation errors. This careful approach finally allows us to comment on the controversial apparent discrepancy between pseudopotential and all-electron *GW* results addressed in several recent studies [1,2]. For the example of silicon, we demonstrate that the inclusion of a much larger number of unoccupied states and the elimination of linearisation errors both contribute to an increase of the band gap. While a certain deviation from pseudopotential calculations remains, it is smaller than previously claimed, and both results lie in comparable proximity to the experimental value.

We benefitted from intensive discussions with T. Kotani and G. Bihlmayer on this subject. This work was funded by the Deutsche Forschungsgemeinschaft (SPP 1145) under the Priority Programme 1145.

[1] W. Ku and A. G. Eguiluz, Phys. Rev. Lett. **89**, 126401 (2002).
[2] M. L. Tiago, S. Ismail-Beigi and S. G. Louie, Phys. Rev. B **69**, 125212 (2004).

Local atomic order and optical properties in amorphous and laser-crystallised GeTe with ab initio methods

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[2]*Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, France*

In this work we present optical spectra calculations for crystalline and amorphous GeTe, a prototype phase-change material. Recent experimental data reveals that GeTe exhibits a profound change in local atomic order upon the phase transition from the crystalline to the amorphous state. Based on these findings a simple structural model of amorphous GeTe was constructed to perform ab initio ground-state and excited-state calculations to reveal the change in optical properties. The optical spectra are calculated in the random-phase approximation. The eigenvalues are corrected with the *GW* approximation and two-particle excitations are taken into account within the framework of the Bethe-Salpeter equation. The results are in good qualitative agreement with experimental data and furthermore explain the profound change in absorption upon amorphisation. It is found that the change in optical absorption is correlated to a change in the local atomic order.

Silicate chain formation in the nanostructure of cement-based materials

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The present works reports our findings arising from ab initio calculations on the stability of silicate chains which aim to shed light on the silicate chain formation in the nanostructure of cement-based materials. Our ab initio study focuses on the growth and merging of silicate chains, which could improve our understanding of the cement-hydration process. It also addresses the pivotal role of certain ionic species on the chain-forming mechanisms. In particular, our results predict the empirically observed rule of number of silicon atoms in the silicate chains ($m = 3n - 1$, m being the number of silicon atoms with $n = 1, 2, \ldots$) and confirm the experimental evidence that dimers arise from a growth mechanism and pentamers from a merging process. Besides, we demonstrate that charged chains are predominant over neutral species at equilibrium. These results will lead to a better understanding of the cementitious matrix nanostructure formation and are a strong basis to improve the mechanical and durability properties of cement-based materials. Furthermore, the implications and the scope of our findings can be easily transferred to other similar systems and materials, such as clays, porous silicate materials, sol-gel materials and more generally any silicate-based materials.

A TDDFT-based formalism for the response of solids, nanostructures and biomolecules

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We will review the recent implementations of TDDFT to study the optical absorption of biological chromophores, one-dimensional polymers and layered materials. In particular we will show the effect of electron-hole attraction in those systems. We will follow two routes: one based on solving the Bethe-Salpeter equation and the other on an orbital-dependent OEP method on top of the GW approximation for the self-energy. Virtues and deficiencies of both methods will be illustrated. In particular we will illustrate a new implementation of the adiabatic-connection fluctuation-dissipation theorem (ACFDT) to treat correlation effects within a (time-dependent) density-functional-based appproach (TDDFT). In this approach, the correlation energy is calculated from the knowledge of the interacting density response. We will make links to the linearised Sham-Schlüter equation that determines the exchange-correlation potential with the electron self-energy of many-body perturbation theory. Both approaches are equivalent, however the numerical implementation is different. We will show some results for the structural properties of simple solids (Si, NaCl) and layered systems. For the latter there are evident discrepancies between the KS and the TDDFT binding energies. This is due to the presence of long-ranged correlations that cannot be described at all by mean-field approximations. All these effects are illustrated taking as example hexagonal boron nitride, where all the structural properties including phonon frequencies are very well described by this approach. We will also show how exchange-correlation kernels with the proper q-dependence can be obtained from this approach and how they can be used to unify many-body and TDDFT-based schemes. Applications to Si and LiF would be used as examples of the theory.

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A TDDFT study of excited states of DNA bases and base assemblies

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We present the results of an investigation of optical absorption spectra of DNA bases and base pairs, carried out by means of time-dependent density-functional theory calculations. The spectra for the isolated bases are compared to available theoretical and experimental data and used for assessment of the method. A particular attention is placed to the relative role of hydrogen-bonding and π-stacking in the modification of optical fingerprints.

An ab initio theory of transport using TDDFT and nonequilibrium Green functions

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We present an ab initio theory for describing the motion of interacting electrons through nanoscopic constrictions. Our theory is based on time-dependent density-functional theory (TDDFT) and nonequilibrium Green functions. We consider the electrode-device-electrode system initially contacted and in equilibrium, therefore the scheme is thermodynamically consistent. Besides the steady-state responses one can also calculate physical dynamical responses. We show that the steady-state current results from a dephasing mechanism provided the electrodes are macroscopic and the device is finite. In the dc case, we obtain a Landauer-like formula when the effective potential of TDDFT is uniform deep inside the electrodes. A computationally tractable scheme is also presented. We first extract the set of initial states by diagonalising the spectral function in the device region. These states will then be propagated in time with proper transparent boundary-condition at the device/electrode interface. This is possible due to a new modified Crank-Nicholson algorithm that allows an efficient time-propagation of open quantum systems. We illustrate the method in one-dimensional model systems as a first step towards a full first-principles implementation.

Ab initio study of the excited-state properties of liquid water

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In the last decades, we have witnessed an increasing interest on water and many studies on the geometry and ground-state properties have appeared in the literature. Nevertheless, its excited-state properties have not been investigated yet. We present here ab initio calculations, in the framework of many-body Green's function formalism, of liquid water. We use snapshots taken from classical molecular dynamics as input geometries for the study of the electronic and optical spectra. The excitation spectra are first obtained within the density-functional theory (DFT) and then corrected within the GW approximation. We obtain an average HOMO-LUMO gap of 4.85 eV at the DFT-LDA level, in good agreement with

previous calculations. The electronic gap is then modified by the GW corrections up to 9.0 eV. The optical absorption spectra are calculated by solving the Bethe-Salpeter equation; they result modified, with respect to the DFT spectra, suggesting the presence of important excitonic effects at low energies.

GW and beyond

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The GW approximation is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W. It may be thought of as exact exchange (Hartree-Fock), together with a partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ, the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as GW. In applying GW to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ is particularly important: G_0W_0, GW_0 and fully self-consistent GW, where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. Our recent formulation [1] of the conductance of a nanosystem which permits the inclusion of electronic correlation effects in time-dependent DFT and GW-like frameworks. I shall also present early results [2] from an approach to vertex corrections in order to include correlation beyond the GW level.

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[2] M. Stankovski and R. W. Godby (to be published).

Fully self-consistent *GW* calculations for atoms and molecules

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We want to emphasise the importance of electron correlation in single-molecule charge and energy transport. To satisfy the conservation laws, we have to use a Φ-derivable scheme. For this, we use a self-consistent Green's function, obtained from the Dyson equation, to calculate the self-energy and to construct the screened interaction W, within the Φ-derivable GW approximation. The self-consistent equations were solved in time-space, in a basis of Slater functions, using finite temperature formalism. We have applied this scheme to calculate total energies of atoms and diatomic molecules. These are, to the best of our knowledge, the first self-consistent GW calculations for total energies of atoms and molecules. We also show that these total energies are very close to the energies obtained from Luttinger-Ward functional, with simple input Green's functions.

Beyond the *GW* approximation

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Band structures are routinely calculated from static density-functional theory, but there is no theoretical foundation for interpreting the calculated one-electron energies as real excitation energies—and the agreement is often quite poor. Not even within time-dependent density-functional theory does one yet have a direct way of obtaining one-electron excitation energies. Instead, such energies are traditionally calculated from many-body perturbation theory (MBPT). Within MBPT, the so-called *GW* approximation (GWA) proposed by Hedin and others in the mid sixties has been remarkably successful for obtaining band structures and band gaps in a variety of different systems. The GWA is a simple extension of the Hartree-Fock method in which the bare Coulomb interaction is screened by the dielectric function of the system and where the latter is usually calculated at the level of the RPA. Despite its well known advantages, the GWA has a number of deficiencies. Most notable is perhaps its inaccurate description of satellite structure. Less well known is the fact that band widths obtained from the GWA are consistently too large compared to experiment in most materials. And there are reasons to believe the GWA to be totally inadequate in cases where the electrons are strongly correlated. What is left out of the GWA is, per definition, referred to as vertex corrections and correspond physically to, e.g., the attraction of the outgoing electron by the hole left behind in a photoemission process. There is thus a strong need to go beyond the GWA and include such effects.

We have previously shown how to construct conserving approximations to response functions within TDDFT. Such approximations necessarily include vertex effects. As it turns out, such conserving response functions allow for the extraction of approximate vertex functions which are local in space and time and which can be used to construct improved electronic self-energies beyond the GWA. We here test some self-energies obtained along these lines and we conclude that this is not an adequate procedure due to the very nonlocal character of a true vertex. We here suggest a cure for this problem based on the observation that, in localised systems, an expansion order by order in the Coulomb interaction seems preferable to infinite summations of particular sets of Feynman graphs. Combining this with the necessity to screen the long-range part of the Coulomb interaction in extended systems leads to the proposal to split the Coulomb interaction in two parts, one weak long-ranged part and a second, strong and short-ranged part. We then screen the long-ranged part as within the GWA and go to second order in the short-ranged part. We hope to be able to present some preliminary results of this new method at the meeting.

Quasiparticle self-consistent *GW* method

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We present some progress in our “quasiparticle self-consistent *GW* (QPsc*GW*) method” based on the all-electron, full-potential LMTO method [1]. The object of the QPsc*GW* method is to obtain the (nonlocal but static) one-body Hamiltonian H_0 (or G_0) which best describes the quasiparticles (QP). The *GW* approximation generates the Green function G as a functional of any given H_0. In QPsc*GW*, this H_0 is choosen self-consistently so that the QP part in G is well reproduced by H_0. The QP from H_0 can be used directly within the one-particle picture to evaluate quantities, e.g., in the construction of the Boltzmann equation.

We applied our QPsc*GW* to a wide range of materials. Our results show systematic improvement over LDA and one-shot *GW* from LDA. As recent results, we will mainly show these points.

1. Theoretical justification:
   The self-consistency of QPsc*GW* does not require a total-energy minimization but the stability of the ground state by H_0 as for the QP excitations. We define a kind of norm $||G^{-1} - G_0^{-1}||$ and discuss that its minimization can approximately give the fundamental equation of the QPsc*GW*.
2. ϵ_∞ vs. band gap:
   QPsc*GW* tends to give somewhat larger band gaps than experiments. The tendendency is sytematic,

and the difference may be because we do not include electron-hole correlation in the dielectric function.

3. f-systems:
   We applied QPscGW to f-systems like Gd, GdN, ErAs and CeO_2. We will discuss trends of these result.
4. Spin susceptibility (in progress):
   We will show results of the spin susceptibility of Ni and Fe based on QPscGW.

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Electronic structure of Cu_2O within self-consistent GW

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It is known that Kohn-Sham density-functional theory (DFT) experiences dramatic problems with d electrons in solids. In particular, it fails to predict a gap in various insulating oxides like CuO. Cu_2O seems to be a good starting point to address the fundamental issue of $3d$ electrons in metal oxides. This semiconductor material has indeed a cubic structure, a closed d shell, and is nonmagnetic. We carried out a study of the electronic structure of Cu_2O within DFT, and then within the GW approximation [1], based on pseudopotentials plus plane-waves basis set. We showed that the GW approximation using the standard technical approximations unexpectedly fails concerning the band gap of Cu_2O, even when the semicore states are properly included in the GW calculation [2]. We therefore performed a self-consistent GW calculation on Cu_2O, using the constrained self-consistent scheme of Faleev *et al.* [3]. We show that small changes in the wave functions can produce large changes in the Hartree potential that are mainly compensated by the changes in the exchange operator. The band gap comes out in good agreement with experiment. Furthermore, when the self-consistent GW band structure and screened Coulomb interaction are used in the solution of the Bethe-Salpeter equation, one obtains a very good optical absorption spectrum compared to experiments, although the optical absorption spectrum of Cu_2O is complex, with several exciton series.

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Merging first-principles and model approaches: GW+DMFT

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First-principles calculations reveal a lot more details about the system than model calculations can hope to do. On the other hand, model approaches are often theoretically more sophisticated than first-principles approaches. By combining the GW method and dynamical mean-field theory (DMFT), which is traditionally applied to study strongly correlated systems in the model context, we obtain a first-principles scheme that incorporates the strength of DMFT in treating systems with strong onsite correlations. In this scheme, the Hubbard U is calculated self-consistently and the so-called double counting is taken into account properly. The new scheme was tested in ferromagnetic nickel with encouraging results.

Hedin's equations and enumeration of Feynman diagrams

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To evaluate dressed correlators for interacting fermions, one must sum over classes of diagrams of all orders of perturbation theory in v. It might be useful, or at least interesting, to know in advance how many diagrams are required at each order of the approximation, and how many are left out. The counting problem is much simpler and is obtained by translating the recursive equations at hand to zero dimensions. I show how Feynman diagrams can be enumerated for the exact theory and GWA starting from Hedin's equations [L. G. Molinari, Phys. Rev. B **71**, 113102 (2005)]. The vertex equation is first written in terms of the Hartree propagator g, in place of the full one. In $d = 0$ four Hedin's eqs. become algebraic, with variables g and v, and the functional derivative is an ordinary one. After removing i factors and replacing (-2) with a parameter ℓ that counts the same loops, they are: $G = g + g\Sigma G$, $W = v + v\Pi W$, $\Sigma = GW\Gamma$, $\Pi = \ell G^2\Gamma$ and $\Gamma = 1 + g^2\partial\Sigma/\partial g$. By searching solutions as a series in the variables v and ℓ, one obtains coefficients that count all Feynman graphs, with weight one, that contribute to a perturbative order (the power of v), with a given number of fermionic loops (the power of ℓ). Omission of vertex corrections makes the number of diagrams grow with a power law, instead of factorially. For example, the numbers for the self-energy are ($x = g^2 v$):

$$\begin{aligned}\Sigma/vg &= 1 + (2+\ell)x + (10 + 9\ell + \ell^2)x^2 + (74 + 91\ell + 23\ell^2 + \ell^3)x^3 \\ &\quad + (706 + 1063\ell + 416\ell^2 + 46\ell^3 + \ell^4)x^4 + \dots \\ &= 1 + 3x + 20x^2 + 189x^3 + 2232x^4 + 31130x^5 + \dots\end{aligned}$$

(at order v^3 (x^2-term) there are 20 diagrams: 10 with no fermion loop, 9 with a single loop and 1 with two loops),

$$\begin{aligned}\Sigma_{GW}/vg &= 1 + (1+\ell)x + (2 + 4\ell + \ell^2)x^2 + (5 + 15\ell + 9\ell^2 + \ell^3)x3 \\ &\quad + (14 + 56\ell + 56\ell^2 + 16\ell^3 + \ell^4)x^4 + \dots \\ &= 1 + 2x + 7x^2 + 30x^3 + 143x^4 + 728x^5 + \dots\end{aligned}$$

The high-density electron gas and the peculiarities of its reduced densities, its self-energy and the Hugenholtz–van Hove identity

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The long-range Coulomb repulsion makes the correlation energy e_c and its kinetic and potential components, t_c and v_c, as well as μ_c, the correlation contribution to the chemical potential, logarithmically divergent for $r_s \to 0$, namely $e_c \to a \ln r_s$, $t_c \to -a \ln r_s$, $v_c \to 2a \ln r_s$, $\mu_c \to a \ln r_s$ with $a = (1 - \ln 2)/\pi^2$ [energies in a.u.]. This is known from the seminal work of W. Macke [1], from the virial theorem and from the definition of μ. It is shown which peculiarities of the momentum distribution $n(k)$ and of the static structure factor $S(q)$ cause the divergent behavior of t_c and v_c, respectively [2]. μ_c is related to the correlation part of the self-energy $\Sigma_c(k, \omega)$ through the identity $\mu_c = \Sigma_c(k_F, \mu)$. Therefore the small-$r_s$ behavior of $\Sigma_c(k_F, \mu)$ is studied with the help of the Gell-Mann/Brueckner trick [3]. It is shown that the GW approximation yields the correct result $a \ln r_s$ for $G \to G_0$ and W within RPA screened Coulomb repulsion. Contrary to this, using G = Green's function of the interacting system and $W \to$ bare Coulomb repulsion gives higher-order terms $\propto r_s(\ln r_s)^2$ and $\propto r_s \ln r_s$ [4] beyond the correct asymptotics $a \ln r_s$.

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Many-body properties of a jellium slab

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The study of many-body properties of jellium in geometries different from the bulk one is a fruitful current subject of research: for example, surface image states and resonances have recently been investigated for a small jellium cluster and for a semi-infinite one, respectively. In this work we study metallic jellium slabs of different thickness. As a starting method we use DFT in the LDA. In this framework we compute the bulk and surface contributions to the total energy, which display a good accord with earlier estimates. Individual kinetic, Coulombic and exchange-correlation contributions to the total surface energy (surface tension) oscillate as a function of the slab thickness, with nontrivial phase relations. A detailed analysis reveals the origin of these oscillations and their link with the surface dipole layer originated by the charge spill-out. Next we treat the eigenvalues of the system, resolved in the wave vector ($\vec{k}_{\|}$) parallel to the surface. The many-body solution, worked out in the GW approach and in the plasmon-pole approximation for the dielectric function, modifies the behaviour obtained in the LDA. As also found for bulk jellium, the dispersion is nonparabolic. At variance with the bulk case, we observe small gaps (~ 0.3 eV) opening at the Fermi energy in the $\vec{k}_{\|}$ dispersion. The origin of these gaps is presently unknown but may be due to an imperfect cancellation of corrections in the numerical GW implementation.

Lifetimes of Shockley electrons and holes at the Cu(111) surface

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A theoretical many-body analysis is presented of the electron-electron inelastic lifetimes of Shockley electrons and holes at the (111) surface of Cu. For a description of the decay of Shockley states both below and above the Fermi level, single-particle wave functions have been obtained by solving the Schrödinger equation with the use of an approximate one-dimensional pseudopotential fitted to calculations and experiment indicates that inelastic lifetimes are very sensitive to the actual shape of the surface-state single-particle orbitals beyond the $\bar{\Gamma}$ ($\mathbf{k}_{\|} = 0$) point.

First-principles description of transport including electron correlation

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The field of nanotechnology has undergone a remarkable growth in the last few years. This development has been fueled by the expectation that unusual properties of matter, which become evident as the size of the structural components of a device shrinks below 10–100 nm, may be exploited. In this work, we first

present an original approach to the calculation of ballistic transport properties of nanostructures from first principles. Then we move beyond the mean-field approach, by addressing the effect of electron-electron interactions on coherent electronic transport through nanoscale conductors. The study of the coherent transport is based on a matrix Green's function methodology, as implemented in the WanT code (freely available at http://www.wannier-transport.org). The approach adopts the maximally localised Wannier functions as basis set. In the case of electron-electron correlated systems, the standard Landauer approach breaks down, and a more general theory is needed to evaluate the electronic transport properties. For this purpose, we derive a generalised Landauer-like expression for the current, valid also in the e-e interacting case. We focus on the strong e-e correlation regime. We apply the above described method to a range of nanosized conductors such as molecular bridges, free-standing and substrate-supported atomic chains. We discuss electronic and linear-response transport properties in the mean-field and interacting case.

GW approximation for correlated systems within the multiple-scattering theory

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The ab initio study of semiconductors and insulators as well as systems with strongly localised electrons entails great difficulties involved by the treatment of excitation energies and many-body effects. The most successful first-principles method, the density-functional theory (DFT) within the local-spin-density approximation (LSDA), is designed for ground-state properties and can not provide a proper description of band structures of semiconductors and insulators. If some localised electrons are present in the system, like $3d$-electrons in the transition-metal oxides, the local-density approximation can be essentially improved by the so-called self-interaction correction (SIC). In this approximation the self-interaction of single-particle charges, which are present in the LSDA, can be canceled out for the localised electrons. However, the self-interaction correction within the LSDA is still not sufficient for a proper description of the excitation energies and band gaps. It is possible to do accurately from first principles by solving Hedin's set of equations for the full Green's function. The implementation of this formalism is very difficult, one neglects commonly the vertex correction (the random-phase approximation), and the self-energy is calculated in this case within the so-called GW approximation. The non-self-consistent GW approximation was successfully implemented within several first-principles methods, but most of the existing implementations are generally designed for systems with delocalised (fast) electrons.

Here we present a general ab initio approach designed for the study of electronic properties of solids, in which on base of the Korringa-Kohn-Rostoker (KKR) method we implemented the self-interaction correction for strongly localised electrons and the non-self-consistent GW approximation for the inclusion of many-body effects. We illustrate our approach by the electronic structure study of some semiconductors and transition-metal oxides.

Wave-function-based determination of the quasiparticle band structure of solids and polymers

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By exploiting the predominantly local character of electron correlation it is possible to set up schemes which allow to determine the ab initio many-body wave function of excited electron-hole and attached electron states of solids and other periodic systems by means of quantum-chemical post-Hartree-Fock correlation methods such as multi-reference configuration interaction (MR-CI). Two different approaches will be presented. The first is a divide-and-conquer algorithm which is based on a strictly local representation of the many-body Hamiltonian of the system by means of suitable localisation schemes. The individual matrix elements of this local Hamiltonian can be obtained from fragment calculations. Diagonalising that local Hamiltonian directly yields the band structure of the systems under consideration with the electron correlation effects being fully included on the quantum chemical level chosen for the fragment calculations. The second approach is an efficient Green's function formalism which effectively sums up infinitely many proper self-energy diagrams. It is implemented with Gaussian-type basis functions. Locality is exploited by representing all quantities in terms of localised Wannier functions and consequently applying spatial configuration selection schemes. The two methods turned out to yield very similar correlated band structures, and the calculated band gaps are found to be much better than those extracted from Hartree-Fock or Kohn-Sham orbital energies.

Investigations using the pseudopotential SIC-LSDA method into the role of n-type defects in DMS ZnO:Co

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We discuss results from ab initio density-functional theory (DFT) calculations using the pseudopotential SIC-LSDA (pseudo-SIC) method of Filippetti et al. [1] to investigate the possible role of n-type native defects in the DMS behaviour of dilute (3%) Co-doped ZnO. We find that the pseudo-SIC method overcomes the major shortcomings of the local-spin-density approximation (LSDA) in describing ZnO:Co viz., the band-gap error and incorrect positioning of Co 3*d*-levels. Results obtained within this improved description for ZnO:Co in the presence of zinc interstitials (I_{Zn})/oxygen vacancies (V_O) suggest that the centres responsible for long-range ferromagnetism in ZnO:Co might be defect-dopant pairs such as I_{Zn}-Co and/or V_O-Co.

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Self-interaction-corrected (SIC) pseudopotential for Ti and TiO$_2$

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We have studied the phase diagram of titanium metal and dioxide by means of ab initio total-energy calculations in DFT-LDA with pseudopotentials. The phases of interest for titanium metal are the α phase (hcp), the high-temperature phase β (bcc) and the high-pressure phase ω (hex); for TiO$_2$ the rutile phase (stable) and the anatase phase (metastable). With the pseudopotential method we have to separate core electrons (treated within the frozen-core approximation) from valence electrons (explicitly treated). However titanium, a transition element, has semi-core electrons. These semi-core states are atomic-like, but their exchange interaction with valence electrons is important. Stabilisation between the different phases changes a lot depending on whether or not we include the semi-core states, whereas structural properties (equilibrium volume and bulk modulus) are only slighthly perturbed. Thus in standard calculation with semi-core states in the valence, the ω phase is more stable than the α phase and the anatase phase more stable than the rutile phase, contrary to the experimental results. Furthermore other problems appear without semi-core states, e.g., for electron energy-loss spectra [1]. In order to correct the LDA error on localised states as the semi-core states, we have introduced an atomic SIC (self-interaction correction) at the level of our pseudopotential in the spirit of [2]. We have extended the formalism to allow one to take into account several orbitals per angular momentum. We present the method developed and discuss the results obtained for the first time on a transition metal and its oxides.

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Orbital- and energy-dependent exchange-correlation functionals

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Orbital- and energy-dependent functional have raised considerable interest recently, because they are potentially able to overcome limitations of commonly used approximations like the local-density approximation, the generalised-gradient approximation or hybrid methods, especially in the description of Van der Waals forces. We show that density-functional theory within the random-phase approximation (RPA) for the exchange-correlation energy provides a correct description of bond dissociation in H_2 in a spin-restricted Kohn-Sham formalismn, i.e., without artificial symmetry breaking. However, the RPA dissociation curve displays unphysical repulsion at larger but finite bond lengths. We also calculate the band-gap energy of a solid using the RPA and find that it is similar to the one obtained from nonrenormalised GW calculations, non-self-consistently, i.e., the G_0W_0 approximation. This provides a well-defined and meaningful interpretation to G_0W_0 quasiparticle band-gap calculations but questions the physics behind the renormalisation factors in the expression of the band-gap energy.

A novel generalised Kohn-Sham scheme

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Generalised Kohn-Sham (GKS) theory [1,2] provides a variety of possible generalisations of the well-known Kohn-Sham implementation of density-functional theory for the calculation of total energies of systems of interacting electrons such as molecules and solids. We present an assessment of various GKS schemes for a one-dimensional model semiconductor and a three-dimensional spherical system. Comparison is made with previous quantum Monte Carlo calculations [3] and with previous *GW* calculations within many-body perturbation theory for these systems. Further *GW* calculations suggest a new GKS approach based on a *GW* formulation of the total energy, which will lead to a new version of density-functional theory for efficient practical calculations which circumvents the problem of approximating the usual Kohn-Sham exchange-correlation energy functional.

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Density-functional theory for superconductors: Applications to MgB_2, Pb and solids under pressure

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Understanding and predicting the properties of superconductors is of both fundamental and technological importance. The discovery of superconductivity in MgB_2, with its rather high critical temperature

($T_c = 39.5\,\mathrm{K}$) and the presence of multiple gaps, has renewed the interest for conventional, phonon-driven superconductors. In this talk, we present several applications of a novel approach to superconductivity that allows one to calculate material-specific properties, such as the gap and the T_c, in a truly ab initio fashion without using any adjustable parameter, such as the Coulomb pseudopotential μ^*. Within this approach, alternative to the Eliashberg theory, we obtained the T_c and the two gaps of MgB_2 in good agreement with experiment, taking into account the anisotropy of this material. As a further application, solving a fully k-resolved gap equation, we found the presence of two gaps also for Pb, due to a different electron-phonon coupling in the two bands crossing the Fermi level. Finally, we have studied the behaviour of T_c in Li and Al as a function of pressure. Despite their simple metal structure, these two materials show a different behaviour upon pressure. While Li undergoes several transitions favouring superconductivity, in Al the electron-phonon coupling decreases with pressure, leading to a complete suppression of superconductivity around 8 GPa.

Abstracts of Posters

Ultra-nonlocality in the TDDFT and MBPT description of quantum transport

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Our recently developed linear-response formulation for conductance [1] is particularly suitable for TDDFT and MBPT analysis. Our first system to study is the interacting homogeneous electron gas (HEG). We can express the change of the conductance of the interacting HEG with respect to that of the noninteracting HEG directly in terms of the exchange-correlation kernel within the TDDFT, or alternatively, via the irreducible polarisation within the MBPT. Assuming that the conductance of the interacting HEG does not change, we derive a restrictive conditions on the form of the exchange-correlation kernel at small wave vector and small imaginary frequency. In particular, we find that a frequency-dependent ultra-nonlocal term needs to be present within the f_{xc}. We generalise the ultra-nonlocal HEG kernel for an inhomogeneous gas and compare the predictions of our approach to the estimates recently obtained within time-dependent current-density-functional theory [2].

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The physics of CdSe nanocrystals

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In the past years, nanometer-sized CdSe clusters have attracted a large interest from the community. These nanocrystals can be prepared with a very narrow size distribution and have found important applications as chemical markers. In most experiments, the nanocrystals are formed by kinetically controlled precipitation and are terminated with capping ligands (e.g., the TOPO molecule) which provide stabilisation of the otherwise reactive dangling orbitals at the surface. Of course, when unsaturated bonds exist, they drive strong reconstructions which modify the electronic properties. However, the extent to which the cluster atomic structure resembles the corresponding bulk, as well as how the reconstruction of the surface affects the electronic properties are not well understood.

We performed extensive density-functional calculations of structural properties and absorption spectra of small CdSe nanocrystals, with a diameter ranging from 0.5 to 1.5 nm. We considered unsaturated clusters, obtained by structural relaxation of wurtzite bulk-like fragments, clusters whose surface was passivated with TOPO molecules and fullerene-like cages. We found that the unsaturated systems exhibited very strong surface reconstructions. However, by passivating the Cd atoms at the surface with TOPO molecules, the clusters remained bulk-like, even for very small diameters. The optical spectra were obtained within time-dependent density-functional theory. The optical absorption is strongly dependent on the size and the geometrical properties of the clusters. Furthermore, our results allowed us to interpret recent experiments of absorption in CdSe nanocrystals.

Spin-polarisation in metastable deexcitation spectroscopy

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The polarisation of emitted electrons in the deexcitation of metastable helium impinging on metal surfaces is investigated from the theoretical point of view. We calculate the Auger emission rate, considering the He* atom at various distances from jellium surfaces with different work functions. We make use of the embedding Green's function method combined with density-functional theory, which allows us to consider the helium atom over a semi-infinite substrate fully accounting for their mutual interaction [N. Bonini et al., Phys. Rev. B **68**, 35408 (2003)]. We will show that the different degree of spin polarisation in the deexcitation probability on different surfaces is strictly related to the energy position of the $2s$ resonance with respect to the Fermi level of the substrate: The $2s$ level being higher then the Fermi one causes a fairly small magnetisation around He*, giving consequently a weakly polarised signal. On the contrary, a small-work-function substrate leaves the $2s$ level fully occupied, causing a strong polarisation in the emitted electrons. These results are in very good agreement with previous experimental findings.

Electronic properties of thin oxide films

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Ultrathin films have gained large interest over the last years due their current or potential application in catalysis, electronic devices and protective coatings. It is often argued that the structural, elastic and electronic (response) properties of these films may differ noticeably from their counterparts with mesoscopic thickness.

We present density-functional theory calculations for the large-gap oxides α-quartz SiO_2 (amorphous SiO_2 is the gate material in standard silicon-based transistors), α-alumina Al_2O_3 (a common support material in catalysis) and hafnia HfO_2 (a promising candidate for replacing SiO_2 in future nanoscale microelectronic devices). We find that the electronic structure becomes bulk-like for very few atomic layers if the local bonding of the bulk material is preserved. This observation stands in contrast to semiconductors that show quantum-size effects up to the nanometer range. This has important consequences for applications and device design. The results are analysed in view of the localised bonding in these oxides. For SiO_2, quasiparticle corrections in the GW approximation have been calculated. We find size-dependent quasiparticle shifts in qualitative agreement with simple models.

Optical properties of the Si(113) surface

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We have investigated the optical properties of the 3×2 ADI reconstruction (which is the most stable one [1]) of the (113) surface of silicon. The slab used in [1] was reduced in thickness for computational reasons, and tests on the atomic geometry and the electronic structure confirmed the reliability of the new unit cell. For the optical properties we have been calculating the x and y contribution to the imaginary part of the polarisability, from which the RAS (reflectance anisotropy spectra) can be obtained. In order to discriminate the surface contributions a layer-by-layer analysis has been performed. The calculations have been done within the plane-wave pseudopotential approach to the density-functional theory as implemented in ABINIT and TOSCA. The optical properties have been derived using the matrix elements of the momentum operator. Electronic bands and optical properties have been obtained also within a semi-empirical tight-binding approach, allowing a much denser **k**-point sampling.

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Ab initio calculations of layered systems based on C and BN

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We calculate with ab initio methods electronic properties of graphite and hexagonal boron-nitride systems, as well as derived systems (like simple or bilayers). We study the validity of simple models simulating the distance between layers, from the bulk distance to isolated layers. These calculations will allow us to study the influence of the geometry and of the interaction between layers on absorption and electron energy-loss spectra. The band-structure calculations are done using Abinit with *GW* corrections [1]. The spectra are calculated in TDDFT using DP [2].

[1] http://www.abinit.org
[2] http://theory.lsi.polytechnique.fr/codes/dp/dp.html

Ab initio study of optical spectra for oxidised Si(100) surfaces

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The effects of oxygen adsorption on the reflectance anisotropy spectrum (RAS) of reconstructed Si(100)-(2×2):O surfaces at low coverages (0.5–1.5 ML) have been studied by an ab initio DFT-LDA scheme within a plane-wave, norm-conserving pseudopotential approach. At 0.5 ML coverage, oxidising only one of the two dimers does not induce noticeable changes in the surface optical anisotropy. On the other hand, backbond oxidation of each surface dimers is enough to strongly reduce the surface optical anisotropy. Coverages close to saturation (1 and 1.5 ML) have the effect of cancelling the surface anisotropy up to 3 eV, as seen in the experiments.

Performance of *GW* total energies in a simple inhomogeneous benchmark system

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A system of two electrons confined within a sphere constitutes a very simple yet challenging problem where the degree of correlation can be controlled by setting the value of the radius R. Bearing in mind that the performance of GW is subject to errors coming from an incomplete cancellation of self-interaction, we will make a comparative study, with respect to the exact solutions, of the total energies and density profiles. We will present the calculations and the analysis of the results starting from the G_0W_0, then the partially self-consistent GW_0 and finally the completely self-consistent GW level.

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All-electron GW code based on FP-(L)APW+lo

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We report on the development of an all-electron GW code based on the Wien2k implementation of the FP-(L)APW+lo method. The optimised basis [1] for the matrix representation of nonlocal operators allows the inclusion of core and semicore states on the same footing with a reasonable computational cost. To be able to address metallic systems, we extended the linearised tetrahedron method to calculate Brillouin-zone convolutions. The dielectric matrix at the Γ-point in our program is solved analytically instead of being approximated from the surrounding points. The self-energy is calculated from first principles, without relying on the plasmon-pole approximation for the frequecy-dependence of the dielectric function. We show the preliminary results obtained with our code on Si and GaAs. The **q**-dependent integration for metals is tested by comparing the dielectric function for the free electron gas with the standard Lindhard function. Macroscopic dielectric functions including local-field effects are calcuated and compared with the results of other methods and experiments [2].

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Quasi-particle effects in 1D polymer chains: The case of red and blue forms in PDA

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Quasi-1D polymer chains are very interesting systems as quantum-wire models [1]. Moreover, they can be used in optoelectronic applications due to their luminescence properties. Polydiacetylene (PDA) has been synthetised in form of isolated chains [2]. Bulk PDAs are known to exist in either of two electronic structures, so-called red and blue phases, showing intense excitonic absortions near 2.4 and 2.0 eV, respectively. Blue chain fluorescence is extremely weak. On the contrary, red chains have a high fluorescence [2], indicating that the exciton-relaxation scheme has to be very different from the blue one. This scheme is still an open question since experimentally no conformal difference between the two types of chains could be detected yet. It has been postulated that the difference between both forms could come from a tilting of the building units giving an identical mean structure. As a first step to the comprehension of PDA isolated chains and crystal structures, we will present a *GW*-BSE study on the evolution of the quasiparticle energies as well as optical excitations as a function of the tilting angle between building units.

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Ab initio calculation of the spin susceptibility for real materials

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The magnetic response of a material to an applied field is the key quantity to understanding its magnetic behaviour. A thorough characterisation is a prerequisite for the selection of optimal materials for modern technological applications in the field of magneto-electronics and spintronics with ever smaller sizes and switching times. The change in magnetisation $\vec{m}(\vec{r},t)$ with respect to an external magnetic field $\vec{B}(\vec{r}\,',t')$ is given by the dynamic spin susceptibility. Of particular interest is the transverse component $\chi^{-+}(\vec{r},\vec{r}\,';\omega)$, because its spectral function reveals the energy and lifetime of spin excitations, which correspond to poles in the complex frequency plane. It can be understood as describing the propagation of an additional spin under the influence of its interaction with the rest of the system. Despite the importance for real-world applications, theoretical studies are still mostly based on simple lattice systems with empirical parameters, such as the Heisenberg model, due to the complicated exchange and correlation effects in solids. Constrained density-functional theory can give some information about the adiabatic regime, but dynamic properties like excited-state lifetimes are only accessible within a more general framework like many-body perturbation theory or time-dependent density-functional theory. The feasibility of both approaches has been successfully demonstrated for spin excitations in simple systems [S. Y. Savrasov, Phys. Rev. Lett. **81**, 2570 (1998); K. Karlsson and F. Aryasetiawan, Phys. Rev. B **62**, 3006 (2000)], but so far there exists no universal implementation capable of describing on an ab initio basis the spin susceptibility of more complex materials like multi-component devices or surfaces.

As a first step towards a full ab initio treatment, we investigate the magnetic response function at the level of the Kohn-Sham susceptibility. This approach is inherently dynamic and already gives a good account of single-particle spin-flip processes on an eV energy scale, the so-called Stoner excitations. Our implementation is based on the full-potential linearised augmented plane-wave (FLAPW) method. We illustrate the performance by applications to different magnetic materials. In the future, we intend to enhance our calculations by including dynamic exchange-correlation effects, which give rise to collective excitations like spin waves in the low-energy part of the spectral function.

During the work we benefitted from intensive discussion with T. Kotani on this subject.

EXCITON: A many-body code interfaced to CRYSTAL

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CRYSTAL is a well-known Hartree-Fock (HF), density-functional theory (DFT) and hybrid HF/DFT code which exploits space-group symmetry to a high degree, which makes calculations on large unit cells feasible. EXCITON is a Gaussian-orbital many-body code interfaced to CRYSTAL. The present version of EXCITON may be used to perform *GW* and Bethe-Salpeter calculations using a plasmon-pole approximation for the dielectric function. Band-structure and optical excitation spectra for solid Ne and Ar computed using EXCITON are presented. Real-space algorithms used in CRYSTAL for computing operators are now being implemented in EXCITON and this will allow many-body calculations to be performed on larger unit-cell systems using either a DFT, hybrid HF/DFT or HF mean-field Hamiltonians.

Band gaps in pseudopotential self-consistent *GW* calculations

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For materials which are incorrectly predicted by density-functional theory to be metallic, an iterative procedure must be adopted in order to perform *GW* calculations. In this paper we test two iterative schemes based on the quasiparticle and pseudopotential approximations for a number of inorganic semiconductors whose electronic structures are well known from experiment. Iterating just the quasiparticle energies yields a systematic, but modest overestimate of the band gaps. Iterating the quasiparticle wave functions as well gives rise to an imbalance between the Hartree and Fock potentials and results in band gaps in far poorer agreement with experiment.

One- and two-photon absorption spectra of carbon nanotubes

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Coulomb interactions are significantly enhanced in low-dimensional systems and are known to give rise to peculiar phenomena of central importance for applications. Quasi-one-dimensional single-walled carbon nanotubes are therefore thought to be dominated by electron-electron interactions, even if their optical spectra have often been interpreted in terms of van Hove singularities so far. In the present work the optical properties of large-diameter SWNTs have been investigated from first principles with the inclusion of excitonic effects. We employed an original symmetry-based approach [1] to implement a state-of-the-art formulation based on many-body perturbation theory. Both self-energy corrections to the single-particle energies and excitonic effects are incorporated, allowing for direct comparison with experiment. Taking advantage of the screw-symmetry of the system, we may afford calculations on tubes with more than a hundred of atoms per unit cell, otherwise unfeasible in standard approches. In addition, this picture gives a more complete understanding of the excited-state properties, of the degeneracies and group character of the single-particle bands and of the selection rules involved in determining optical spectra. We computed one- and two-photon absorption spectra, achieving excellent agreement with recent experiments [2]. We discover that for all the tubes studied, excitonic effects are very strong, with binding energies ranging beetween 0.3 and 0.9 eV, and crucial in both the peak shapes and positions.

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Spin-dependent *GW* approximation

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Effects due to collinear and noncollinear spin polarisation as well as spin-orbit coupling play an important role in many solid-state systems containing transition metals or heavy elements, respectively. We examine the consequences of including these effects in the system of Hedin's equations. For this purpose we extend the existing theory using Schwinger's functional-derivative formalism to a Hamiltonian with an external magnetic field and the spin-orbit coupling term. The expression for the self-energy is approximated in GW. A discussion will be given, which physical effects can be described within such an approximation and which lie beyond the GW approach. Additionally, the spin structure of the Bethe-Salpeter equation for the polarisation function in the spin-polarised case is studied. In order to illustrate the analytical results we apply the formulas in the case of collinear spin polarisation to the antiferromagnetic insulator MnO. We perform a spin-polarised density-functional calculation using the generalised gradient approximation and the projector-augmented-wave method to obtain band structures. They are improved by adding quasiparticle shifts. The screening is described by means of a model dielectric function, including a simplified treatment of the dynamical effects.

Self-energy of nickel oxide in spin-polarised GW approximation

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NiO is a prototypical strongly correlated magnetic insulator. As is well known, DFT treatments of such systems suffer from the notorious band-gap problem. GW corrections improve the situation but do not in general give full agreement with experiment. Beginning with a hybrid DFT-HF Hamiltonian, we calculate the self-energy of NiO in the spin-polarised GW approximation, using an all-electron basis of localised Gaussian orbitals and a plasmon-pole approximation to the dielectric function. Varying the amount of Hartree-Fock exchange in the initial calculation allows us to tune the quasiparticle band gap to its exact experimental value, whilst the inclusion of RPA screening in GW yields corrections to the relative positions of energy bands which are not present at the mean-field level. This approach may also prove useful in tackling other strongly correlated transition-metal oxides.

Quasiparticle calculations of high-k-material band offsets with silicon

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The size reduction of MOS transistors requires the usage of alternative materials as gate oxide layers. In this work we have studied the energy-band alignments of a high-dielectric material, namely, $ZrSiO_4$ in contact with Si. We have used first-principles DFT calculations within the local-density approximation. The many-body corrections were included as calculated by the GW approximation. The calculated band offsets were found to be 2.03 and 2.28 eV for VBO and CBO, respectively. This result suggests that $ZrSiO_4$ can be a promising candidate to replace SiO_2 in future MOSFET technology.

Electronic deexcitation by intervalley scattering: Ab initio study in GaAs and GaP

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In a number of semiconductors under strong electric field, the carriers can be scattered from the conduction-band minimum to energetically higher satellite minima ("valleys"). These processes are accompanied by the emission and absorption of short-wave phonons ("intervalley phonons"). Intervalley scattering plays an important role in many phenomena such as absorption of light in indirect semiconductors, relaxation of electrons after pulsed optical excitations, negative differential resistance and Gunn effect [1,2]. This is why the corresponding electron-phonon interaction parameters, the intervalley deformation potentials, are of particular interest in the characterisation of optical and transport properties of semiconductors and heterostructures designed to have many-valley band structure.

In this work we calculate, in the framework of density-functional perturbation theory [3], the intervalley deformation potentials in GaAs and GaP. We consider scattering between high-symmetry points as well as in arbitrary directions in the Brillouin zone. Our results show very strong dispersion and anisotropy of the deformation potentials, which depend on the wave vectors of the initial and final electronic states. So, we find a qualitative agreement with previous theoretical results of Ref. [4], in which the empirical pseudopotential method and rigid-ions model were used. Quantitatively, however, our results are very different from the results of Ref. [4]. Finally, we show how to calculate the contribution of intervalley-scattering times to the lifetime of the electronic excitation and compare our preliminary results to available experimental and theoretical data [4,5].

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Nonlocal vertex corrections in Hedin's equations

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Many-body perturbation theory provides a potentially powerful class of orbital-functional methods, which may be implemented within Kohn-Sham theory, generalised Kohn-Sham theory or other frameworks. For their successful implementation it is essential to have adequate and tractable models for the self-energy. A nonlocal operator like the self-energy can be consistently calculated through many-body perturbation theory. We are implementing local and nonlocal vertex corrections in Hedin's equations and are investigating various quantities which have to be adequately described if such a model is going to be successful in fully self-consistent calculations. So far these quantities have been the static structure factor, the pair-correlation function and the spectral function of the homogeneous electron gas. We also hope to present total-energy calculations. The effect of a local vertex correction on jellium is investigated and results are used to determine a tractable model self-energy.

Electronic excitations: Ab initio calculations of electron energy-loss spectra

N. Vast, L. Dash, F. Bruneval, V. Quequet and L. Reining
Laboratoire des Solides Irradiés, CEA-CNRS UMR 7642, Ecole Polytechnique, 91128 Palaiseau, France

In this work, we address the question of the theoretical prediction and interpretation of experimental spectra obtained by the excitation of valence electrons, such as valence photoemission spectra, electron energy-loss spectra (EELS) or absorption spectra, or by deexcitation of an incoming electron into the conduction band, like in bremsstrahlung isochromat spectroscopy (BIS). We particularly expose the case of the transition metal oxides ZrO_2 [1,3], TiO_2 [2,3] and Cu_2O [3], and compare our theoretical results with experimental data. In ZrO_2 [3], we show which levels of theory are appropriate, starting either from the density of occupied or empty states or from the joint density of states obtained from ground-state density-functional calculations, to the effect of the inclusion of matrix elements of the dipolar operator (random-phase approximation RPA) and the inclusion of off-diagonal elements in the response function (RPA with crystal local-field effects). Additional exchange and correlation local fields within the adiabatic time-dependent local-density approximation and many-body effects in the quasiparticle and in the TDDFT frameworks [4,5] are presented in order to explain the reasons why the RPA turns out to be a level of approximation appropriate for electron energy-loss spectroscopy, in those materials as well as in a test case like bulk silicon.

This research was supported by the joint research program "ISMIR" between CEA and CNRS. Computer time has been granted by CEA/DSM on the cluster of Compaq Alphaserver (project p543) and NEC SX6 (project p93) and by IDRIS on the NEC SX5 (project 544). We acknowledge support from EU's 6th Framework Programme through the NANOQUANTA Network of Excellence (NMP4-CT-2004-500198).

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Strong field ionisation using time-dependent density-functional theory

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Time-dependent density-functional theory appears to be a valuable tool to study multiphoton ionisation of atoms or molecules. However, some difficulties appear for high laser intensities, when multiple ionisation becomes possible. Photoionisation of atoms, submitted to an intense laser pulse, is studied within this framework. In order to gain some insight in the dynamics of the process, the kinetic-energy spectra of the emitted electrons are analysed. Particular attention is paid to the problem of determining the photoelectron spectra, as no direct physical meaning can be attributed to the electronic orbitals in DFT calculations. A method to calculate the spectra, based on the electronic density only, is proposed.

Time-dependent quantum transport in 1D model systems with electron-phonon interactions

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We investigate the role of phonons in the time-dependent current response of one-dimensional systems. A finite (central) chain described by the Holstein model is contacted to the left and to the right with two semi-infinite free-electron leads. We consider different phonon-couplings in the chain, namely strong vs. weak regimes. We drive the whole system out of equilibrium by exposing the electrons to an external time-dependent electric field. The influence of the leads is taken into account via an exact embedding scheme, and the central system is evolved by treating the phonons in the semi-classical limit. By studying the time-dependent current in different points of the chain, we provide some generic remarks about the influence of the phonon-electron interaction on both the transient and steady-state regime.

Dynamic structure factor of silicon: RPA, *GW*-RPA and TDLDA calculations and inelastic X-ray-scattering experiments

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Our recent work shows excellent agreement between the dynamic structure factor of Si as measured by inelastic X-ray scattering and the result of standard TDLDA. TDLDA reproduces the shape, position and intensity of the experimental results. Small discrepancies arise on the high-energy side of the spectrum [1]. In the present contribution we compare the spectra calculated within RPA, *GW*-RPA and TDLDA in order to illustrate the question up to which degree many-body effects are contained in the TDLDA exchange-correlation kernel. The results are compared to the literature [2] as well as to the experiments which have been carried out in parallel. We analyse not only the overall shape and position of the plasmon peak but also secondary structures on the plasmon. Possible implications for the application of the *GW* approximation are discussed.

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Wojciech Wełnic	RWTH Aachen, Germany
Ludger Wirtz	Université des Sciences et Technologies de Lille, France
Paul Ziesche	MPI für Physik komplexer Systeme, Dresden, Germany

6 General Workshop/Conference Announcements

6.1 XRMS 2005

X-Ray Spectroscopy of Magnetic Solids

Villigen PSI, Swithzerland
October 18th - 20th, 2005

Scope

XRMS 2005 brings together leading scientists in the field of spectroscopy of magnetic solids using X-rays. It will provide a stimulating forum to present new ideas, discuss future perspectives, and establish new collaborations.

Location

Paul Scherrer Institut
5232 Villigen PSI
Switzerland

For more informations see: http://xrms2005.web.psi.ch/ .

6.2 11th International Conference on Theoretical Aspects of Catalysis (ICTAC-11)

Teikyo University, German Campus, Schmöckwitz near Berlin
June 11-14, 2006

The ICTAC-11 meeting will be organized jointly by Klaus Hermann (Theory Department, Fritz-Haber Institute, Berlin) and Joachim Sauer (Quantum Chemistry Group, Humboldt University, Berlin). It continues a worldwide series of meetings which are held biennially and address recent theoretical developments and applications of theoretical methods to problems of catalytic relevance with special focus on heterogeneous catalysis. While the subject attracts mostly researchers with theoretical background emphasis is also put on the interaction between theory and experiment. Therefore, a few invited lectures given by selected high-caliber experimentalists are always included in the program. The present list of keynote speakers includes

- A. Bell, University of California, Berkeley (USA)
- G. Ertl, Fritz-Haber Institute, Berlin (Germany)
- G. Kresse, University of Vienna, Wien (Austria)
- U. Landman, Georgia Tech, Atlanta (USA)
- M. Mavrikakis, University of Wisconsin, Madison (USA)
- Y. Morikawa, Osaka University, Osaka (Japan)
- J. Norskov, CAMP Technical University, Lyngby (Denmark)
- P. Saalfrank, University of Potsdam, Potsdam (Germany)
- M. Scheffler, Fritz-Haber Institute, Berlin (Germany)
- R. Schlögl, Fritz-Haber Institute, Berlin (Germany)
- B. Smit, University of Amsterdam, Amsterdam (The Netherlands)
- W. Thiel, MPI for Carbon Research, Muehlheim (Germany)
- P. Ugliengo, University of Torino, Torino (Italy)
- E. Wang, Chinese Academy of Sciences, Beijing (China)
- T. Ziegler, University of Calgary, Calgary (Canada)

There will also be about 12 invited talks of younger outstanding scientists (to be announced).

The meeting can accommodate up to 100 participants who are welcome to submit abstracts for poster or oral presentations (20 mins). The number of oral presentations is limited and decisions of acceptance will be made based on quality and suitability.

For further details and pre-registration please consult the web at

http://www.fhi-berlin.mpg.de/ICTAC-11/

For the organizing committee,

Klaus Hermann, Joachim Sauer

6.3 Tutorial on quantum simulations of solids and liquids

CECAM, Lyon, France

November 7, 2005

A tutorial on "Quantum simulations of solids and liquids" will be given at CECAM starting November 7. It is for PhD students. CECAM provides financial support for travel and accommodation. If there are interested persons, please, register as soon as possible. Number of places is limited. There are already many applicants. But applications are still accepted, though a decision will be taken soon.

For more information please see

`http://www.cecam.fr/index.php?content=activities/tutorial&action=details&wid=23`

7 General Job Announcements

Postdoctoral Position

Virtual Materials Laboratory

Department of Materials Science and Engineering

Delft University of Technology
The Netherlands

Two years' postdoctoral position is available at the Virtual Materials Laboratory, Department of Materials Science and Engineering, Delft University of Technology, the Netherlands.

The project aims at the design of stable metal-hydrides that can be applied as membranes for hydrogen gas separation. The main part of the research involves thermodynamic calculations (cluster variation method) combined with dft calcaulations to obtain insight in the phase stability range of metal alloys. In particular the influcence of order of metal and interstitial atoms on the stability will be investigated. This is of vital importance for the mechanical properties and liftime of the membranes. In addition some experimental investigation of phase stability and crystal structure will be performed in cooperation with the Netherlands Energy Centre.

Requirements: Ph.D. in phyiscs, chemistry, or materials science.

Candidates with a strong background and interest in thermodynamics, computer simulations (ab initio DFT), or solid state physics are invited to contact:

Dr. A. (Amarante) J. Böttger, TU Delft,
Rotterdamseweg 137, 2628 AL Delft, Netherlands
A.J.Bottger@tnw.tudelft.nl
Tel: +31 (0)15-278-2243

Post-Doctoral Research Assistant in Computer Simulation of Materials

School of Physical Sciences
University of Kent at Canterbury, UK

A postdoctoral position is available in the simulation-based applications group at the University of Kent. The position is funded by the European-Union INTERREG programme, and offers an outstanding opportunity to pursue internationally-leading research using atomistic computer simulation methods. The project aim is to expand a "Virtual Centre of Excellence" in this research in the S.E. England-North France European region, making outreach to academic partners and work on industrially-relevant problems priorities. Within this remit the successful candidate will have considerable freedom to pursue his/her chosen research goals. These are likely to overlap with some of the group's interests which include nanostructured materials, interfaces, surfaces and surface processes, low-dimensional systems, transport, defects and electronic-physical structure relationships. This is a European venture involving the Universities of Kent, Littoral (Dunkirk) and Picardie (Amiens), and there is ample funding for exchange visits. We have excellent local computing facilities and extensive access to a range of national supercomputers.

You should have a Ph.D. and experience in computer simulation techniques in physics, materials science or theoretical chemistry. Experience with first-principles (DFT) methods is particularly welcome. Knowledge of French would be helpful, but is not essential. For more information on applying, and to make informal enquiries, contact Dr. Philip Lindan (p.lindan@kent.ac.uk).

See

http://www.kent.ac.uk/physical-sciences/fmg/samba/index.htm

for an overview of our activities.

The post is for two years, the second by mutual agreement. Salary will be in the range £19,460 - £29,128 per annum on the salary scale Research Assistant Grade 1A.

Postdoctoral Position

CEA-DAM Île-de-France, France

"Atomistic based constitutive description for energetic crystals"

A lot of the thermodynamic and chemical properties of a solid explosive are attributable to the mesoscopic characteristics of the compound. On the other hand, in situ experimental observations at the mesoscopic scale are very difficult in shock or detonation conditions. Thus, mesoscopic models are mainly based on theoretical and numerical micrsocpic analyses.

So, we propose to use large scale molecular dynamics simulations of energetic crystals subjected to quasi-static and dynamic loading in order to provide specific information regarding plastic deformation and localisation phenomena in those materials and next the influence of such processes on the chemical properties. The long term goal is to produce the key elements of an anisotropic, rate dependent constitutive model suitable for use in mesoscale simulations, with emphasis on HMX, TATB and simple polymeric materials as binder. Particular attention will be given to identification, characterisation, and quantification the unit processes by which localisation occurs ; and to the role of defects (dislocations, voids, inclusions, and grain boundaries) on the material response.

The work will be made at CEA-DAM Ile-de-France, in France, near Paris. The contract is for one year renewable once (i.e. two years maximum). Net salary would be around 2100 euros a month. Applicants should send their CV and letters of reference to:

Laurent Soulard

CEA - DAM - Île-de-France
BP12
91680 Bruyéres-le-Châtel
Tel: 01 69 26 73 38
laurent.soulard@cea.fr

EXPERT IN COMPUTATIONAL MATERIALS SCIENCE

(Scientist, permanent position)

at the Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, Germany

The position will become available in 2006.

Requirements:

1. PhD, preferably in physics, strong background in condensed matter theory
2. Experience with ab-initio and atomistic simulations
3. Ability for independent research activities and for team work
4. Experience with acquisition of external funding and projects, and with supervising of graduate and PhD students

Activities:

1. Modelling and computer simulation of materials modification by particle irradiation, investigations on the change of structural, electronic and magnetic properties
2. Improving the basic understanding of the evolution of radiation defects and of ion-beam-assisted engineering of nanostructures and thin films
3. Collaboration with experimentalists in the framework of internal and external research projects
4. Arranging, acquiring and operating projects based on external funding

Further information: Prof. Wolfhard Möller, Dr. Matthias Posselt

E-mails: w.moeller@fz-rossendorf.de, m.posselt@fz-rossendorf.de

Phone: +49 (0)351 260 2245, +49 (0)351 260 3279

http://www.fz-rossendorf.de/FWI

Ph.D. Positions in Santa Barbara and Berlin

One or more PhD positions in Computational Materials Physics are available in the Materials Department at the University of California, Santa Barbara, and in the Fritz Haber Institute, Berlin. Projects involve first-principles calculations for bulk and surface defects for materials that may include wide-band-gap semiconductors and oxides. The students will work jointly with Prof. Chris Van de Walle and Prof. Matthias Scheffler, who is a Distinguished Visiting Professor at UCSB. Candidates should have excellent grades and a keen interest in materials physics and a motivation to interact with experimentalists. The work may be done partly in Berlin and partly in Santa Barbara. Applications should include: (1) Curriculum Vitae, (2) One-page summary of research goals and accomplishments to date, (3) Names and contact information (including email) of three references.

More information about the University of California, Santa Barbara, and about the Materials Department can be found respectively at

http://www.ucsb.edu

and

http://www.materials.ucsb.edu.

Information about the Van de Walle and Scheffler research groups can be found respectively at

`http://www.mrl.ucsb.edu/~vandewalle`

and

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

For more information or to apply, please contact Prof. Chris Van de Walle (vandewalle@mrl.ucsb.edu) or Prof. Matthias Scheffler (scheffler@fhi-berlin.mpg.de).

Postdoctoral Position at UC Santa Barbara

The Materials Research Laboratory at the University of California, Santa Barbara, is starting a new research emphasis on metallic nanoparticles embedded in semiconductors for novel electronic applications. A postdoctoral position in computational materials is available to work jointly with Profs. Nicola Spaldin and Chris Van de Walle. The project involves calculations based on density-functional theory and related methods, and will involve close collaboration with synthetic chemists and device physicists. Topics to be investigated include ErAs/GaAs interfaces and heterostructures, growth of nanoislands, and the exploration of alternative rare-earth/group-V binary compounds (NdN, GdN, etc). Candidates should have experience with electronic structure theory and condensed matter theory. Applications should include: (1) Curriculum Vitae, (2) Publication List, (3) One-page summary of accomplishments to date, and their significance, (4) Names and contact information (including email) of three references.

More information about the University of California, Santa Barbara, and about the Materials Research Laboratory can be found at

http://www.ucsb.edu/

and

http://www.mrl.ucsb.edu/ .

Information about the Spaldin and Van de Walle research groups can be found at

`http://www.mrl.ucsb.edu/~nicola`

and

`http://www.mrl.ucsb.edu/~vandewalle`.

Deadline for applications is October 15, 2005.

For more information or to apply, please contact

Prof. Chris Van de Walle (vandewalle@mrl.ucsb.edu)
Materials Department
University of California
Santa Barbara, CA 93106-5050
Ph.: (805) 893-7144
Fax: (805) 893-8983

Post-doctoral Position in Theoretical Solid State Physics
University of Erlangen-Nürnberg, Germany

A post-doctoral position in theoretical solid state physics is available in the solid state theory group at the University of Erlangen-Nürnberg, Germany.

The research project comprises the density-functional-theory studies of the electron correlation effects on surfaces. The project also involves a study of electron excitations in a framework of time-dependent density functional theory. In particular, the SiC surfaces and interfaces with metals and semiconductors will be investigated. An experience in computational solid state physics is required and a knowledge of DFT and many-body theory is desired.

The salary is at the BAT IIa level common at German public universities.

For further information visit our website at

http://www.tfkp.physik.uni-erlangen.de/.

The position is immediately available. Further inquiries and applications (including a CV, names and addresses of three references and list of publications) should be directed to Prof. Dr. Oleg Pankratov (Oleg.Pankratov@physik.uni-erlangen.de).

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http://www.tfkp.physik.uni-erlangen.de/

Computational Chemistry/Physics Postdoc

National Renewable Energy Laboratory
Golden, Colorado, U.S.A.

We invite applications for a postdoctoral researcher in the Computational Sciences Center at the National Renewable Energy Laboratory. The successful candidate will work closely with chemists, physicists, computational scientists, and mathematicians to develop new mathematical and computational methodologies capable of designing and searching for materials with relevant properties using atomistic electronic structure methods and statistics-based methods.

Applicants must have a recent PhD in computational chemistry/physics, computational material science, or related field. Experience in electronic structure methods or statistics-based discovery, interest in algorithmic/mathematical development, and scientific programming ability in Fortran or C is required. Knowledge of solid-sate chemistry and semiconductor physics is desired.

For detailed information on this position see

`http://www.nrel.gov/hr/employment/rpp/jobs_files/6087.html.`

NREL is the U.S. Dept. of Energy's premier laboratory for renewable energy and energy efficiency and we are located just south of Boulder and west of Denver. More information on the research activities at NREL can be found at

http://www.nrel.gov.

Please submit your resume and cover letter (reference REQ# 5300-6087) by email, to: `Beverly_Maestas@nrel.gov`.
NREL Human Resources, 1617 Cole
Blvd., Golden, CO 80401.

NREL is an equal opportunity employer committed to diversity.

Postdoctoral or Research associate position
in NREL's solid state theory group: Nanostructures, Alloy Theory and PV materials

National Renewable Energy Laboratory (NREL)
`http://www.sst.nrel.gov`

NREL's Solid State Theory Group is looking to fill a Postdoctoral or Research Associate position. The research areas include theory of nanostructures, alloy theory, defect physics in solids and photovoltaic materials. The positions are for up to 3 years. The salary range is $48,000- $62,000 per year, depending on seniority, qualification and experience. Applicants are expected to have a strong background in solid-state theory. The positions are with Alex Zunger, Solid State Theory Group Leader. The start date is between January 2006 and summer 2006. Applications are being considered now. For more details about ongoing work, see `http://www.sst.nrel.gov`.

The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists. The group has outstanding computational facilities, an excellent basic-research atmosphere, and is located in the beautiful Rocky Mountains. Consult our web page for additional information on the group, its history, research subjects, publications, current and past personnel and facilities.

Interested candidates should send **immediately** curriculum vitae, list of publications (including preprints of unpublished papers if possible), and arrange for two to three references addressed to:

Alex Zunger, M/S 3213
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401

Clarification or further details can be obtained via email to `alex_zunger@nrel.gov`

NREL is an equal opportunity employer and proud of its commitment to diversity. Women and minorities are encouraged to apply.

POSTDOCTORAL RESEARCHER POSITION

Lawrence Livermore National Laboratory

Applications are invited for a postdoctoral research position to perform first-principles simulations of the optical properties of semiconductor nanomaterials. We are seeking candidates with experience performing electronic structure calculations and an interest in applying these techniques to study technologically relevant materials. The candidate will join a collaborative research project involving Lawrence Livermore National Laboratory, University of California at Davis and industry.

Suitable candidates should have a PhD in condensed matter physics or materials science, or related disciplines, have experience with density functional calculations and with high performance computing. The candidate will be required to interact closely with other members of the project, including experimentalists synthesizing nanomaterials.

The position is available immediately and will last for two years.

Applications and requests for more information should be sent to:

Dr. Giulia Galli
Lawrence Livermore National Laboratory
Livermore, CA 94550
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galli@llnl.gov

Lawrence Livermore National Laboratory is an Affirmative Action / Equal Opportunity Employer.

Postdoctoral Research Associate in Theoretical Condensed-Matter Physics

Department of Physics, University of York, U.K. and Nanoquanta Network of Excellence

Applications are invited for a position, based in York, within the EU-funded Nanoquanta Network of Excellence (Nanoscale Quantum Simulations for Nanostructures and Advanced Materials), which consists of 10 European research groups and over 100 researchers.

A two-year postdoctoral position is available to carry out research in electronic spectra, lifetimes, transport and total energies for advanced materials and nanostructures, and to support the research integration of the NANOQUANTA network. A PhD in theoretical condensed-matter physics and experience of ab initio computational work are essential.

Starting salary in the range £21,640 - £29,128 p.a. The post is fixed-term for up to 2.5 years. Further details of the post and how to apply may be obtained from Prof. Rex Godby (Tel. +44 (0)1904 432231, e-mail: rwg3@york.ac.uk).

http://www.cmt.york.ac.uk/nanoquanta/

`http://www-users.york.ac.uk/~rwg3/`

Assistant Professor in Computational Condensed Matter Physics

Department of Physics, New Jersey Institute of Technology, Newark, USA

A position is open for a tenure track Assistant Professor of Physics in the area of Computational Condensed Matter Physics. The candidate will be expected to teach undergraduate and graduate physics courses and develop an independent and rigorous research program based on strong external funding. Candidates are being sought who have experience in the development of new an novel techniques for understanding the properties of correlated electron systems and more general multifunctional materials.

Please provide a complete set of documents (PDF files). These include:

1. Cover Letter
2. Current version of CV with all Publications
3. Research Statement and Research Plan
4. Teaching Experience and Teaching Statement/Philosophy
5. List of References

Send document by e-mail (pdf files) to tyson@adm.njit.edu .

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Postdoctoral Position
Department of Physics, King's College London, U.K.

A three-year postdoctoral position is available at the Department of Physics of King's College London, to develop hybrid (quantum + classical) techniques and perform calculations in the general field of grain boundary/dislocation interface physics.

Candidates should hold (or should soon hold) a Ph. D. in the field of atomistic modelling of materials. The appointment is available between now and February-March 2006.

Besides myself in the computational modelling group of the Physics Department, King's College London, the members of the (EPSRC Materials Modelling Programme) project team include N.Fleck, V.Deshpande, J.Willis and M.Ashby from Cambridge and A.Cocks from Leicester, as well as an extended group of external collaborators/advisers abroad (E.Artz, R.Car, P.Castenada, A.G.Evans, J.W.Hutchinson, A.Needleman).

A full description of the position with details on how to apply can be found in

http://www.jobs.ac.uk/jobfiles/HY850.html

For further details please write to me at

`alessandro.de_vita@kcl.ac.uk` .

Alessandro De Vita
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King's College London
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Postdoctoral Position

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

”Efficient implementations of new exact-exchange based DFT functionals and GW for solids”

A postdoctoral position is available in the Theory Department at the Fritz-Haber-Institut in Berlin on the description of advanced materials from first principles. The objective of the proposed project is to develop efficient algorithms for exact-exchange based functionals and the GW-method and to implement them into existing electronic structure codes for applications to semiconductors, transition metal compounds, metal oxides, their surfaces and defects within them.

The postdoctoral position is funded through the Network of Excellence (NoE) Nanoscale Quantum Simulations for Nanostructures and Advanced Materials (NANOQUANTA, for more details see

http://www.cmt.york.ac.uk/nanoquanta/).

The PostDoc will be strongly involved in the accomplishment of the integration activities of the NoE, more specifically the Integration of Theory and Code Development as well as Training and Reach-Out. The scientific part of the project will be carried out in collaboration with the other network nodes. The group is also closely collaborating with the University of California in Santa Barbara (UCSB) and short research stays (2-3 months) at the UCSB will be encouraged. The position is initially for two years and can be extended.

Applicants for this position should hold a PhD in a natural science and should have a strong background in electronic-structure calculations. Programming experience is desirable. Interested candidates should send their curriculum vitae, highlighting their main achievements and experience, together with a publication list to the address given below. Electronic applications are welcome, and reference letters will be given proper consideration. Please feel free to send an e-mail for informal inquiries. Applications are accepted until the position is filled.

Dr. Patrick Rinke
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
14195 Berlin, Germany
E-mail: rinke@fhi-berlin.mpg.de

Further information about the group can be found at

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

Three Month Marie Curie Host Fellowship for a Ph. D. Student

Disciplines
Physics: Condensed matter properties
Contract Type: 3 months visit in the framework of a Ph. D.
Location : LSI, Ecole Polytechnique, 91128 Palaiseau Cedex, FRANCE
Deadline: 05/10/2005
Start Date: 01/01/2006
Salary: 1200 euros/month
Contact Dr. Christine Giorgetti
CNRS-DR5-LSI
christine.giorgetti@polytechnique.fr

”Ab-initio calculations of many-body effects in electronic spectra”

A Marie Curie host fellowship for PhD students is available at the Laboratoire des Solides Irradies, Ecole Polytechnique, Palaiseau (Paris, France), in collaboration with Dr. Christine Giorgetti in the group of Dr. Lucia Reining. The fellowship is for 3 months. The research will be inserted in the framework of ongoing collaborations within the EU Network of Excellence NANOQUANTA: Nanoscale Quantum Simulations for Nanostructures and Advanced Materials. The overall topic of the network research is the theory of nanometer-scale structures and the spectroscopic processes that can be used to characterize those structures, their electronic and optical properties, and their growth. These are studied using fundamental theory and state-of-the-art ab-initio computer simulations. (Please see also http://www.cmt.york.ac.uk/nanoquanta/). In particular, the group in Palaiseau has been working during the last years in the field of one- and two-particle Green's functions calculations (GW, excitons in optical absorption), and time-dependent density-functional theory. These topics should be developed further, concerning both theory and numerics. Computer codes are already available in Palaiseau. Computational facilities include locally several Compaq DS-25 Workstations, and national supercomputer time.

The project includes the ab-initio calculation of absorption and eels spectra of layered systems like graphene, or hBN based ones. It will focus on interactions between nanostructures through realization of tests and further developments of methods to describe them efficiently. This work will have two components, one numerical and the other theoretical.

The candidate should be working on a thesis subject close to these topics. He/she should have a strong background in theoretical condensed-matter physics including numerics, and should like to perform both analytical and numerical work. As the work will contribute to the nanostructure-related efforts of the NANOQUANTA network, previous experience with nanostructure physics is desirable in order to carry out the project in view of the final applications.

Candidates must be nationals of an EU Member or Associated State, or have resided in the EU for at least five years immediately prior to their application. They must not undertake their fellowship in the country of their nationality or recent center of activity. At the time of selection the candidate must be 35 years old or less.

The position is intended for the duration of 3 months, starting from 01/01/06. The deadline for applying for this position is 05/10/05. Information on the group can be found at http://theory.polytechnique.fr. Contact: Please send your application or questions to christine.Giorgetti@polytechnique.fr.

Contract Type: temporary Position Graduate Number of Positions 1

http://theory.polytechnique.fr/

Dr. Christine Giorgetti
LSI
Ecole Polytechnique
91128 Palaiseau Cedex
FRANCE

POSTDOCTORAL POSITION IN THEORETICAL SOLID-STATE PHYSICS

"Ab initio Calculation of Spin Waves"

Institute of Solid State Research, Research Centre Jülich, Germany

The department Theory I at the Institute of Solid State Research now seeks a motivated postdoctoral researcher to strengthen its activities in the field of magneto-electronics. The goal of this project is the development of an ab initio method to calculate material-specific spin- wave spectra in magnetic solids. As collective modes that carry spin but no charge, spin waves are the agents of magnetisation dynamics and play a crucial role in the design of magnetic storage devices with fast read and write cycles. Due to their collective nature, spin-wave excitations cannot be described within a single-particle picture. The project hence combines density-functional theory with Green-function techniques from many-body perturbation theory to include dynamic exchange-correlation effects in the transverse spin susceptibility, which can be directly related to experimental measurements. The implementation uses the full- potential augmented plane-wave (FLAPW) method.

Candidates should have a Ph.D. degree in physics or a related subject, a background in ab initio electronic-structure methods and good computational skills. There are no nationality or age restrictions. The position is available for two years starting on 1 October 2005, with the actual starting date open to negotiation, and is funded by the German Research Foundation (DFG) through the Priority Programm 1145 "Modern and universal first-principles methods for many-electron systems in chemistry and physics". An extension is possible.

Applications and further informal inquiries should be addressed to

Dr. Arno Schindlmayr
Institut für Festkörperforschung
Forschungszentrum Jülich
52425 Jülich
Germany
E-Mail: A.Schindlmayr@fz-juelich.de

Applications should include a curriculum vitae, a list of publications and a statement of relevant academic experience. Electronic applications are welcome, and reference letters will be given proper consideration. Applications are accepted until the position is filled. Information about the department is provided at

`http://www.fz-juelich.de/iff/e_th1` .

Postdoctoral and Ph.D. Positions in Computational Materials Science

University of Munich, Germany

Applications are invited for a postdoctoral and a Ph.D. position in computational condensed matter physics and materials science.

Postdoctoral position: The work will focus on novel phenomena at oxide interfaces and is part of an international multidisciplinary project within the European Science Foundation (ESF) network. The successful candidate must have a Ph.D. in theoretical or computational physics, chemistry or materials science. We are looking for a highly motivated individual with experience in large scale electronic structure calculations and/or strongly correlated materials as well as the ability to work in an international team and collaborate with experimentalists. The position is expected to start in the beginning of 2006. Initial duration is one year (extendable up to three years).

A PhD position is available to investigate the adsorption on oxide surfaces. The candidate is expected to have a background in condensed matter theory, materials science and preferably experience in electronic structure calculations. The position is available immediately.

Applications with a curriculum vitae, list of publications and statement of research experience and interests and a list of two references should be sent to:

Dr. Rossitza Pentcheva
Department of Earth and Environmental Sciences
Section Crystallography
Ludwig-Maximilians-University
Theresienstr. 41
80333 Munich
Germany
e-mail: pentcheva@lrz.uni-muenchen.de

Postdoctoral Position
Université de Bourgogne – CNRS, Dijon, France

A postdoc position in the field of **computational surface science** is opening in the physical chemistry department of the Université de Bourgogne - CNRS, Dijon, France. The projet is entitled **Multiscale study on the dynamics of nanostructure formation on oxide surfaces: Role of diffusion, reactivity and lateral interactions**.

The position is offered for one year and can possibly be renewed. The starting date should be no later than 1 april 2006. Candidates must not be French nationals and must have never worked in France. They must hold a PhD in chemistry or physics that was obtained less than five years ago. The successful candidate should have worked in condensed matter theory or computational materials science. Experience with density functional or Monte Carlo methods is appreciated. Candidats should send a curriculum vitae and list of publications to one of the two contact persons below. Selection will start immediately and until the position is filled.

Project description:

When atoms are deposited on a surface, they may form various kinds of nanostructures. The great varity of shapes is due to the collectif behaviour of the atoms which develops on a scale of several tens of nanometers. In the proposed project we combine density functional theory (DFT) computations and kinetic Monte Carlo (KMC) simulations in order to bridge the gap between the atomic scale (0.1 nm) where the chemical reactions takes place and the structural scale (10 nm). Using DFT we determine microscopic quantities such as adsorption energies, diffusion barriers and binding energies of small clusters of adatoms. These parameters are then used as input for kinetical simulations. They are carried out within the KMC method, where the atomic mobility and agreagation are described as activated processes with thresholds that depend on the local atomic environment. With this combined, mesoscopic approach we are able to study the influence of experimentally controlled parameters such as temperature, deposition flux and coverage, on the nano-structuring at the surface.

Contact persons:

Dr. Peter Krüger, e-mail: pkruger@u-bourgogne.fr, phone: +33-38039-6155
Dr. Florence Baras, e-mail: fbaras@u-bourgogne.fr, phone: +33-38039-6167
Laboratoire de Recherches sur la Réactivité des Solides (LRRS)
UMR 5613 Université de Bourgogne - CNRS, B.P. 47870, 21078 Dijon, France

40th Anniversary Professorships and Readerships
University of York, UK

The University has recently announced the creation of a number of new Professorships and Readerships, adding to the twenty appointed in 2004.

The Department of Physics strongly encourages applications for these Professorships and Readerships, to be held in any of its research groups Condensed Matter Theory, Nanophysics (Magnetic Materials and Surface Physics), Nuclear Physics and Plasma Physics.

Please see

http://www.york.ac.uk/depts/phys/jobvacs/40thannapp.htm

for details.

The closing date is 19 October 2005.

Postdoctoral Positions

School of Materials Science and Engineering Nanyang Technological University, Singapore

Now I am seeking outstanding applicants for 1 or 2 postdoctoral positions, which could start immediately. I have a high performance computing Rock cluster with 25 nodes (50 CPUs : 3.2GHz). Please allow me to write down some boring technical text just for possible reference. Candidates should have a PhD degree in physics, chemistry, materials science or related disciplines, with experience in first principle computation and molecular dynamics simulation. They will work on polymeric electronics project with experienced experimentalists, which is one of major thrusts in Singapore. The modeling work will be partly in collaboraiton with Prof. William A. Goddard III at Caltech. Salary is commensurate with demonstrated capabilities and experiences. NTU offers an attractive and comfortable living environment.

Haibin Su
School of Materials Science and Engineering
Nanyang Technological University
Block N4.1, Level 1, Room 32
50 Nanyang Avenue
Singapore 639798
Telephone: (65) 6790-4346
Fax: (65) 6790-9081
Email: hbsu@ntu.edu.sg

SHORT TERM POST-DOCTRAL POSITION

Kyoto University, Japan

Subject

A program on computational materials science in Department of Materials Science & Engineering of Kyoto University, Japan has an opening for a Post-Doc scientist to support on-going activities in the group. Design and exploration of advanced materials by means of computational modeling and experimental works are objectives of the group. Intimate collaborations with experimental groups in both academic and industry sites are being constructed. Materials of our interests include electronic, functional, magnetic, structural, energy-storage, catalysis and other kinds of materials.

Conditions

Applicants should possess a Ph.D. in materials science, physics or chemistry and should have a keen interest in computational materials science. Expertise in computational methods such as first principles, molecular dynamics, Monte-Carlo, thermodynamics, etc is desirable. Good communication skill in either English or Japanese is mandatory. The position is available immediately. Appointment will be made until 30th March 2006 in the first instance. It may be continued until 30th March 2007 depending upon mutual agreement and availability of funds. Monthly allowance is in the level of assistant professors in Japanese National Universities, which is determined by her/his personal carrier. Work place is located inside of Kyoto University.

Applications

Candidates wishing to discuss their application should contact

Professor Isao TANAKA
Department of Materials Science and Engineering,
Kyoto University
Yoshida, Sakyo, Kyoto 606-8501 JAPAN
isao.tanaka@materials.mbox.media.kyoto-u.ac.jp
http://cms.mtl.kyoto-u.ac.jp/index-e.html

Applications, including a full CV, a list of publications, an abstract of her/his research achievements (within one page of an A4 sheet), and names and addresses (e-mail) of two referees, should be sent to the above address.

Closing Date: This announcement is valid only until we find an appropriate candidate.

Ph. D. Student Position, Duesseldorf, Germany

A position for a PhD student in the department "Computational Materials Design" at the "Max-Planck-Institute for iron research" in Düsseldorf, Germany is available. The research will be focused on the development and application of ab-initio based multiscale methods to accurately describe structure and electronic properties of interfaces and interfacial defects in modern wide band gap semiconductors.

The main focus will be on nitride-based III-V semiconductors as presently used e.g. to make efficient light emitting devices or as needed for the next generation of DVD players. The research will be performed in close collaboration with experimental and theoretical partners within the EC.

Strong interaction with the other groups is therefore expected. The successful candidate should have a degree in Physics, Chemistry or Materials Science, and have a strong interest on microscopic simulations.

Preference will be given to candidates with strong background in any (or several) of these fields: electronic structure calculations, molecular modeling, density functional theory, or empirical potentials. The position is funded by the European Research Training Network: "Interfacial Phenomena at Atomic Resolution and multiscale properties of novel III-V SEMiconductors" (PARSEM). The position is reserved to citizens of European Union or of an Associated State (Bulgaria, Iceland, Israel, Liechtenstein, Norway, Romania, Switzerland, and Turkey). German citizens or long-term residents are excluded.

Interested candidates should send a CV, list of publications, and name and address (including email) of three references, preferably by email or fax, to

Prof. Jörg Neugebauer
e-mail: neugebauer.at.mpie.de
or
Dr. Liverios Lymperakis
e-mail: lymperakis.at.mpie.de

Postal address:

Abteilung "Computergestütztes Materialdesign"
Postfach 140444
40074 Düsseldorf
Germany

Phone: +49 211 6792-586
Fax: +49 211 6792-465

Postdoctoral Research Associate

”Theory of phase-coherent electronic and photonic systems”

Department of Physics - Lancaster University, UK

Salary: £20,000 - £30,000 pa

Closing date: 10 October, 2005
Starting date: 1 November 2005 or after (latest: 1 March 2006)

Applications are invited for a two-year, fulltime Postdoctoral Research Associate position (with possible extension), funded by the EU Marie Curie Excellence Grant ”Nanoelectrophotonics”. The post-holder will work together with Dr. H. Schomerus on the theory of phase-coherent electronic and photonic systems. Specific projects address the generation of non-classical light, transfer and protection of quantum information, microlasing, and the accentuation of quantum effects in nanoelectronic and nanophotonics systems. The post-holder will enjoy the lively atmosphere at the Lancaster Centre for Nanoscale Dynamics and Mathematical Modelling, which also includes the groups of Dr. V. Cheianov, Prof. V. Falko, Prof. C. Lambert, and Prof. R.Tucker.

Applicants should hold a PhD or equivalent and have an excellent research and publication record in theoretical condensed-matter physics, quantum optics, quantum dynamics, or a related field. Ideally, they would have postdoctoral research experience.

Applications (including CV and list of publications, and supported by two letters of recommendation) should be sent to Dr Henning Schomerus, Physics Department, Lancaster University, Lancaster, LA1 4YB, UK. For informal inquiries, email h.schomerus@lancaster.ac.uk .

8 Abstracts

The high-pressure phase of alumina and implications for Earth's D" layer

Artem R. Oganov (1) and Shigeaki Ono (2)
(1) Laboratory of Crystallography, Department of Materials ETH Honggerberg,
HCI G 515, Wolfgang-Pauli-Str. 10, CH-8093 Zurich, Switzerland
(2) Institute for Research on Earth Evolution,
Japan Agency for Marine-Earth Science and Technology,
2-15 Natsushima-cho, Yokosuka-shi, Kanagawa 237-0061, Japan

Abstract

Using ab initio simulations and high-pressure experiments in a diamond anvil cell, we show that alumina (Al2O3) adopts the CaIrO3-type structure above 130 GPa. This finding substantially changes the picture of high-pressure behaviour of alumina, in particular we find that perovskite structure is never stable for Al2O3 at zero Kelvin. The new phase suggests a re-interpretation of previous shock-wave experiments and has important implications for the use of alumina as a window material in shock-wave experiments. In particular, the conditions of the stability of this new phase correspond to those at which shock-wave experiments indicated an increase of the electrical conductivity. If this increase is due to high ionic mobility in the CaIrO3-type phase of Al2O3, similar effect can be expected in the isostructural post-perovskite phase of MgSiO3 (which is the dominant mineral phase in the Earth's D" layer). The effect of the incorporation of Al on the perovskite/post-perovskite transition of MgSiO3 is discussed.

Published in: Proc. Natl. Acad. Sci., vol. 102, 10828-10831 (2005).
For reprints and additional information contact: Artem R. Oganov (a.oganov@mat.ethz.ch).

Ab initio study of the high-pressure behavior of CaSiO3 perovskite

Daniel Y. Jung and Artem R. Oganov
Laboratory of Crystallography, Department of Materials, ETH Honggerberg,
Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Abstract

Using density functional simulations, within the generalized gradient approximation and projector-augmented wave method, we study structures and energetics of $CaSiO_3$ perovskite in the pressure range exceeding that of the Earth‘s lower mantle (0-150 GPa). At zero Kelvin the cubic (Pm3m) $CaSiO_3$ perovskite structure is unstable in the whole pressure range, at low pressures the orthorhombic (Pnam) structure is preferred. At 14.2 GPa there is a phase transition to the tetragonal (I4/mcm) phase. The $CaIrO_3$-type structure is not stable for $CaSiO_3$. Our results also rule out the possibility of decomposition into oxides.

Published in: Physics and Chemistry of Minerals, v. 32, 146-153 (2005).
For reprints and additional information contact D.Y.Jung (daniel.jung@mat.ethz.ch) or Artem R. Oganov (a.oganov@mat.ethz.ch).

Low-temperature magnetization of (Ga,Mn)As semiconductors

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B.L. Gallagher
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Abstract

We report on a comprehensive study of the ferromagnetic moment per Mn in (Ga,Mn)As ferromagnetic semiconductors. Theoretical discussion is based on microscopic calculations and on an effective model of Mn local moments antiferromagnetically coupled to valence band hole spins. The validity of the effective model over the whole range of doping studied is assessed by comparing with microscopic tight-binding/coherent-potential approximation calculations. Using the virtual crystal $k \cdot p$ model for hole states, we evaluate zero-temperature mean-field contributions to the magnetization from the hole kinetic energy and exchange energies, and magnetization suppression due to quantum fluctuations of Mn moment orientations around their mean-field ground state values. Experimental low-temperature ferromagnetic moments per Mn are obtained by superconducting quantum interference device and x-ray magnetic circular dichroism in a series of (Ga,Mn)As semiconductors with nominal Mn doping ranging from ∼2% to 8%. Hall measurements in as-grown and annealed samples are used to estimate the number of uncompensated substitutional Mn moments. Based on the comparison between experiment and theory we conclude that all these Mn moments in high-quality (Ga,Mn)As materials have nearly parallel ground state alignment.

arXiv:cond-mat/0508255 - 10 Aug 2005
Submitted to Physical Review B
Rreprints available from g.vanderlaan@dl.ac.uk

Point defects in uranium dioxide: ab initio pseudopotential approach in the generalized gradient approximation

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Jean-Paul Crocombette
Commissariat à l'Energie Atomique (CEA), Centre de Saclay,
DEN/DMN/SRMP, Bâtiment 520, 91191 Gif-sur-Yvette, France

Abstract

The stability of point defects in uranium dioxide is studied using an ab initio plane wave pseudopotential method in the Generalized Gradient Approximation of the Density Functional Theory. Uranium pseudopotentials are first tested in both the Generalized Gradient Approximation and the Local Density Approximation on metallic phases of uranium and on uranium dioxide. It is found that the Generalized Gradient Approximation gives the best description of these materials. The energies of formation of point defects (single vacancies and interstitials, Frenkel pairs and Schottky defects) in UO_2 are calculated. The values obtained lead to a reliable set of numerical data that are analyzed in the framework of the Point Defect Model commonly used to assess defect concentrations in uranium dioxide as a function of the stoichiometry. The ability of the Point Defect Model to accurately reproduce defect concentrations in uranium dioxide is discussed.

(To appear in Journal of Nuclear Materials (2005))
Contact person: Preprint available on request: Michel.Freyss@cea.fr

Observation and theoretical description of the pure Fano-effect in the valence-band photo-emission of ferromagnets

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**Institut für Theoretische Physik - Computational Physics,*
Technische Universität Graz, A-8010 Graz, Austria
A. I. Lichtenstein
Institut für Theoretische Physik, Universität Hamburg,
20355 Hamburg, Germany

Abstract

The pure Fano-effect in angle-integrated valence-band photo-emission of ferromagnets has been observed for the first time. A contribution of the intrinsic spin polarization to the spin polarization of the photo-electrons has been avoided by an appropriate choice of the experimental parameters. The theoretical description of the resulting spectra reveals a complete analogy to the Fano-effect observed before for paramagnetic transition metals. While the theoretical photo-current and spin difference spectra are found in good quantitative agreement with experiment in the case of Fe and Co only a qualitative agreement could be achieved in the case of Ni by calculations on the basis of plain local spin density approximation (LSDA). Agreement with experimental data could be improved in this case in a very substantial way by a treatment of correlation effects on the basis of dynamical mean field theory (DMFT).

(Accepted for publication in PRL)
Contact person: Jan.Minar@cup.uni-muenchen.de

Negative spin polarization in Co— $SrTiO_3$—Co magnetic tunnel junctions

J. Velev[1], K. D. Belashchenko[1], D. A. Stewart[2], S. S. Jaswal[1], and E. Y. Tsymbal[1]
[1]*Department of Physics and Astronomy, University of Nebraska,*
Lincoln, NE 68588, USA
[2]*Cornell Nanoscale Science and Technology Facility, Cornell University,*
Ithaca, NY 14853, USA

Abstract

We perform an ab-initio study of the spin-dependent tunneling in epitaxial Co—$SrTiO_3$—Co magnetic tunnel junctions. Structural relaxation shows that Co grows in the bcc structure on top of $SrTiO_3$. We find that the spin polarization of the tunneling current is negative in agreement with experimental data [1]. While the current in magnetic tunnel junctions based on sp-bonded insulators (i.e. such as Al_2O_3 and MgO) is dominated by majority spin carriers, the intricate complex band structure of $SrTiO_3$ enables efficient tunneling of the minority d-electrons from the ferromagnet. Our results indicate that a very large spin polarization can be attained in $SrTiO_3$-based tunnel junctions, which could provide an alternative option for device applications.

This work is supported by National Science Foundation.

[1] J. M. De Teresa, A. Barthélémy, A. Fert, J. P. Contour, R. Lyonnet, F. Montaigne, P. Seneor, and A. Vaurs, Phys. Rev. Lett. 82, 4288 (1999); J. M. De Teresa, A. Barthélémy, A. Fert, J. P. Contour, F. Montaigne, and P. Seneor, Science 286, 507 (1999).

(Submitted to Physical Review Letters)

Contact person: jvelev@unlserve.unl.edu

Structure of terrace steps on As-passivated Si(111): A detailed study by *ab initio* calculations

A. Antons, R. Berger, K. Schroeder
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany
B. Voigtländer
Institut für Schichten und Grenzflächen, and `cni` -
Center of Nanoelectronic Systems for Information Technology,
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Abstract

The structures of terrace steps on As-covered Si(111) are examined using *ab initio* calculations. In STM images two orientations of steps are found to terminate As-covered Si islands after annealing: $(11\bar{2})$ and $(\bar{1}\bar{1}2)$. Total energy calculations and simulations of STM images yield detailed informations on the atomic structures of the steps: In the lowest energy configuration for both orientations surplus As atoms replace any exposed Si atoms at the steps. The As atoms rearrange to establish a threefold coordination. For $(11\bar{2})$ steps the atom positions of the relaxed configuration are very close to the ideal bulk positions, but for $(\bar{1}\bar{1}2)$ steps the terminating As atoms form dimers in front of the steps. The different atomic structures of the two step orientations clearly show up in the simulated STM images for negative bias (occupied states imaged), the STM images for positive bias (unoccupied states) are much less distinctive. All features of existing experimental positive-bias STM images can be explained by an analysis of the electronic local density of states. With the calculated step energies we construct a phase diagram for the equilibrium shape of As-covered islands. In the accessible range of As chemical potentials between As bulk and As_4 molecules we expect either triangular islands terminated by $(11\bar{2})$ steps or hexagons with long edges of $(11\bar{2})$ orientation and short ones with $(\bar{1}\bar{1}2)$ orientation.

(Final version, submitted to PRB, 6 September, 2005)
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Lloyd's formula in multiple-scattering calculations with finite temperature

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Abstract

Lloyd's formula is an elegant tool to calculate the number of states directly from the imaginary part of the logarithm of the Korringa-Kohn-Rostoker (KKR) determinant. It is shown how this formula can be used at finite electronic temperatures and how the difficult problem to determine the physically significant correct phase of the complex logarithm can be circumvented by working with the singlevalued real part of the logarithm. The approach is based on contour integrations in the complex energy plane and exploits the analytical properties of the KKR Green function and the Fermi-Dirac function. It leads to rather accurate results, which is illustrated by a local-density functional calculation of the temperature dependence of the intrinsic Fermi level in zincblende GaN.

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Effect of interface states on spin-dependent tunneling in Fe/MgO/Fe tunnel junctions

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Abstract

The electronic structure and spin-dependent tunneling in epitaxial Fe/MgO/Fe(001) tunnel junctions are studied using first-principles calculations. For small MgO barrier thickness the minority-spin resonant bands at the two interfaces make a significant contribution to the tunneling conductance for the antiparallel magnetization, whereas these bands are, in practice, mismatched by disorder and/or small applied bias for the parallel magnetization. This explains the experimentally observed decrease in tunneling magnetoresistance (TMR) for thin MgO barriers. We predict that a monolayer of Ag epitaxially deposited at the interface between Fe and MgO suppresses tunneling through the interface band and may thus be used to enhance the TMR for thin barriers.

(Accepted for publication in Phys. Rev. B)
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Orbital Polarization in Itinerant Magnets

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Abstract

We propose a parameter-free scheme of calculation of the orbital polarization (OP) in metals, which starts with the strong-coupling limit for the screened Coulomb interactions in the random-phase approximation (RPA). For itinerant magnets, RPA can be further improved by restoring the spin polarization of the local-spin-density approximation (LSDA) through the local-field corrections. The OP is then computed in the static GW approach, which systematically improves the orbital magnetization and the magnetic anisotropy energies in transition-metal and actinide compounds.

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Comparison of the full-potential and frozen-core approximation approaches to density-functional calculations of surfaces

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Abstract

We scrutinize the accuracy of the pseudopotential approximation in density-functional theory (DFT) calculations of surfaces by systematically comparing to results obtained within a full-potential setup. As model system we choose the CO oxidation at a $RuO_2(110)$ surface and focus in particular on the adsorbate binding energies and reaction barriers as target quantities for the comparison. Rather surprisingly, the major reason for discrepan cy does not result from the neglected semi-core state relaxation in the frozen-core approximation, but from an inadequate description of the local part of the Ru pseudopotential, responsible for the scattering of f like waves. Tiny, seemingly irrelevant, imprecisions appearing in these properties can have a noticeable influence on the surface energetics. At least for the present example, we obtain excellent agreement between both approaches, if the pseudopotential describes these scattering properties accurately.

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Curvature effects on vacancies in nanotubes

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Abstract

Vacancies have a strong impact on the properties of nanotubes. We have therefore performed density-functional calculations for achiral single-wall nanotubes(CNTs) with single vacancies. Our calculations show that the curvature in the CNTs facilitates the relaxation leading to a local contraction. The vacancies prefer to align along the tube axis and the formation energy decrease with increasing curvature. The local magnetic moment at the vacancy disappears and the local charging decreases as the diameter of the nanotube gets smaller.

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Surface Electronic Structure of the Fe_3O_4(100): Evidence of a Half-Metal to Metal Transition

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Abstract

In situ prepared Fe_3O_4(100) thin films were studied by means of scanning tunneling microscopy (STM) and photoelectron spectroscopy (PES). The atomically resolved $(\sqrt{2} \times \sqrt{2})R45^\circ$ *wave-like* surface atomic structure observed by STM is explained based on density functional theory (DFT) and *ab initio* atomistic thermodynamics calculations as a laterally distorted surface layer containing iron and oxygen, referred to as a *modified B-layer.* The work-function values of the Fe_3O_4(100) surface extracted from the cutoff of the photoelectron spectra are in good agreement with those predicted from DFT. On the Fe_3O_4(100) surface both the PES measurements and the DFT-results show a strong reduction of the spin-polarization at the Fermi level (E_F) compared to the bulk density of states. The nature of the surface states in the majority band gap of Fe_3O_4 is analyzed.

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Xe adsorption on metal surfaces: First-principles investigations

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Abstract

Rare-gas adsorption on metal surfaces is a classic example of physisorption, in which it has long been assumed that rare-gas atoms would occupy highly coordinated sites. Over the last several years, however, the understanding of even such basic properties as the adsorption site preference and nature of the bonding of these apparently "simple" systems has been called into question. In particular, recent experiments and first-principles calculations have surprisingly shown that for Xe on a variety of metal surfaces, the low coordinated on-top site is preferred over the hollow sites. In the present paper we report in detail the results of our first-principles investigations into Xe/metal adsorption systems which were briefly presented in an earlier publication. We employ the all-electron full-potential linearized augmented plane wave (FP-LAPW) method using LDA and GGA-PBE functionals and investigate Xe adsorption on the Mg(0001), Al(111), Ti(0001), Cu(111), Pd(111), and Pt(111) surfaces in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure. From investigation of the lateral and perpendicular potential-energy surfaces we find that Xe atoms adsorb in the on-top sites in all cases. We identify a noticeable site dependence of the Pauli repulsion, which largely actuates the adsorption site preference. We anticipate that the identified microscopic nature of the binding between Xe and metal atoms may also be generally valid for other rare-gas atom/metal systems.

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Converged properties of clean metal surfaces by all-electron first-principles calculations

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Abstract

All-electron full-potential linearized augmented plane-wave calculations of the surface energy, work function, and the interlayer spacings of close-packed metal surfaces are presented, in particular, for the free-electron-like metal surfaces, Mg(0001) and Al(111), and the transition metal surfaces, Ti(0001), Cu(111), Pd(111), and Pt(111). We investigate the convergence of the surface energy as a function of the number of layers in the slab, using the Cu(111) surface as an example. The results show that the surface energy, as obtained using total energies of the slab and bulk from separate calculations, converges well with respect to the number of layers in the slab. Obviously, it is necessary that bulk and surface calculations are performed with the same high accuracy. Furthermore, we discuss the performance of the local-density and generalized gradient approximations for the exchange-correlation functional in describing the various surface properties.

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Surface Processes and Phase Transitions from *ab initio* Atomistic Thermodynamics and Statistical Mechanics

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Abstract

Knowledge of the surface composition and atomic geometry is a prerequisite for understanding the physical and chemical properties of modern materials such as those used in, for example, heterogeneous catalysis, corrosion resistance, sensors, and fuel cells. To understand the function of surfaces under realistic conditions, it is crucial to take into account the influence of environmental gas at finite (possibly high) temperatures and pressures. Recent experimental and theoretical studies have shown that when transition metal surfaces are exposed to high oxygen pressures, thin oxide-like structures can form which may have little similarity to the bulk oxides, and thus possess unique chemical and physical properties. Given that technological oxidation catalysis typically involves oxygen-rich conditions, such structures may be present, and in fact be the active material for the reaction, as opposed to the traditionally believed pure metal. Using the approach of *ab initio* atomistic thermodynamics, free-energy phase-diagrams for oxygen/transition-metal systems in (T, p)-space ranging from ultra-high vacuum to technically-relevant pressures, p, and temperatures, T, are discussed. In addition, results of *ab initio* statistical mechanical schemes, namely, the Lattice-gas Hamiltonian plus Monte Carlo (MC) simulations, are presented for oxygen/transition-metal and alkali-atom/metal systems, where for the latter, the recently introduced "Wang-Landau" algorithm is employed, which affords an accurate estimation of the density of (configurational) states, therefore allowing a direct determination of all major thermodynamic functions.

Catal. Today 105, 17 (2005)
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9 Presenting Other Initiatives

9.1 Upcoming New Journal ”Fluid Dynamics & Materials Processing”

It is my pleasure to introduce you to the upcoming new journal ”Fluid Dynamics & Materials Processing”. being published by the Tech Science Press.

Please feel free to distribute it to those who might be interested. I hope that you find this new journal and useful to your research.

Further information is on the website:

http://www.techscience.com/fdmp

Thank you for your attention.

Kind regards,

Hiroshi Mizuseki
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10 SCIENTIFIC HIGHLIGHT OF THE MONTH: ”Ab Initio Modeling of Biological Systems”

Ab Initio Modeling of Biological Systems

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Abstract

Biological systems are particularly challenging for ab initio quantum mechanical methods, yet first principles calculations can now tackle problems of great current biological interest, that cannot be solved by a different approaches. Here we outline the state-of-the art of ab initio biological modeling by presenting a brief survey of new trends in the development of algorithms as well as few representative applications.

1 Introduction

One of the goals of modern biology is the understanding of biological phenomena at the molecular level, which involves the study of the structure of biomolecules and their functions. A detailed atomistic investigation of a biological system requires often the knowledge of its electronic structure. For instance, enzymatic reactions are bond-forming and bond-breaking phenomena, that require a quantum mechanical description [1] Another example is represented by photoreceptors (such as rhodopsin [2, 3, 4]), which involve excited states and the interaction between the biomolecules and the electromagnetic field. QM-based approach may be also of invaluable help to correctly describe polarization effects (*e.g.* in ion channels [5]) as well as metallo-proteins, where very subtle chemical phenomena (such as the fact that the metal ion ligand bond has a partially covalent nature) play an important role. Finally, QM calculations allows for comparison with a variety of spectroscopic data, such as IR [6, 7, 8, 9, 10], Raman [11, 12], and NMR [11, 13], which can be obtained from the electronic structure calculations without additional assumptions.

The study of biologically active molecules from first principles, such as proteins and DNA, however poses its own unique set of problems. Biological systems present an extremely high degree of complexity. First of all, proteins may contain several hundreds of amino acids, *i.e.* thousands of atoms. Secondly, biological processes occur in aqueous solution and span millisecond or even seconds time scales. In addition, very often solvent molecules have an active role and have to be explicitely considered. Furthermore, dynamical effects both on short and long time scales are extremely important and must be taken into account in biological modeling. Therefore, the overall accuracy and predictive capability of computational models for biological systems are limited by (i) the accuracy to which relevant phase space regions are sampled, (ii) the degree to which the microscopic system on the computer reflects the typically macroscopic system in nature, and, in addition, (iii) the accuracy to which interaction forces are described.

Despite the explosive growth of computer power over the past two decades has led to the development of large-scale simulation techniques, direct application of first principle approaches to the study of biomolecules, although important, is still limited for the size of the model system that can be studied [14, 15, 16]. Few noticeable exceptions are represented by very recent studies on DNA [17, 18]. A successful strategy is represented by the coupling of multi-nanosecond classical molecular dynamics (MD) simulations [19, 20] based on empirical force fields to hybrid quantum mechanical/molecular mechanics (QM/MM) [21] optimizations and/or MD simulations. In a typical protocol classical MD is used to sample the relevant conformational space of the system and then QM/MM calculations are performed on representative configurations, where the region of interest, *e.g.*, the active site of an enzyme, is treated at QM level. This approach has been widely used in many studies [1, 3, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31].

Here we shall summarize some of the most common techniques used in the ab initio modeling of biological systems, namely density functional theory and the so-called hybrid QM/MM methods (section 2). Subsequently, we illustrate the power of the methodology for the modeling of biological systems by a survey of selected very recent applications from our and other groups. This survey is clearly very limited in scope and cannot cover important contributions from several active groups. For a more exhaustive reviews, see, e.g. Refs. [1, 32, 33]. First, we shall discuss fully ab initio calculations on a solvated DNA filament, which represent some of the biggest calculations ever performed on a biological system [17, 18] (section 3.1). Then, we will show the power of the combined use of classical and hybrid QM/MM simulations to the study of enzymatic catalysis, taking as illustrative example the decarboxylation of orotidine 5′-monophosphate by orotidine 5′-monophosphate decarboxylase [28] (section 3.2.1). Finally, we illustrate an extension to this approach to the excited-state dynamics of the retinal protonated Schiff base in rhodopsin [3] (section 3.2.2). Then we conclude with some final remarks (section 4).

2 Computational tools for atomistic biomodeling

2.1 Quantum mechanical methods

Because of the large number of atoms that must be explicitely taken into account (> 50-80) when dealing, for instance, with an active site of an enzyme, it is prohibitive the use of post-Hartree-Fock methods [14, 15, 16]. For this reason the most common method applied to biological systems is density functional theory (DFT), which achieves good accuracy and efficiency in large scale systems. A detailed description of DFT can be found in Ref. [34].

Large-scale DFT calculations on biological system are often performed with a plane wave (PW) basis set. Although localized basis sets require fewer basis functions per atom than PW, in a Kohn-Sham scheme the computational cost scales linearly with the number of PW, whereas with a localized basis set the cost scales as the cube of the number of basis functions. PW offer further advantages: (i) convergence can be easily monitored increasing the number of PW (which depends on only one parameter, *i.e.* the cut-off energy); (ii) forces in a PW calculation are not affected by Pulay terms; (iii) a PW basis set is completely unbiased and, therefore, no basis superposition error is present. Calculations with PW can practically deal only with valence electrons and pseudo potentials for the core electron must be used. The most common pseudopotentials are the norm-conserving pseudopotentials of Troullier and Martins [35], and Goedecker, Teter and Hutter [36], and the ultra soft non-norm-conserving pseudopentials due to Vanderbilt [37].

A promising valid alternative to pure PW calculations is represented by hybrid Gaussian and plane waves (GPW) method [38, 39]. The GPW method provides an efficient way to treat the Hartree (Coulomb) energy and the orthogonalization of the wave functions. These terms are notoriously not scaling linearly with system size, and they dominate the computational cost for larger systems in standard electronic structure calculations. The GPW method uses an atom-center Gaussian-type basis set to describe the wave functions, but uses an auxiliary plane waves basis (PW) set to describe the density. With a density represented as PW on a regular grid, the efficiency of Fast Fourier Transform can be exploited to solve the Poisson equation and to obtain the Hartree energy in a time scale that scales linearly with the system size. Some applications based on this method have appeared in the literature [40, 41, 42, 43, 44].

In a DFT calculation a crucial role is played by the choice of the exchange and correlation functional. Although the simple local density approximation (LDA) is extremely good for studying solids, it does not give reasonably good bonding energy and lengths and other molecular properties. Therefore, when dealing with biological systems, it is necessary to go beyond LDA and use a gradient corrected functional. One the the most common functionals used in biomodeling is the one that uses the Becke exchange [45] and the Lee, Parr and Yang correlation [46], or BLYP. BLYP functional gives a quite accurate description of hydrogen-bonded systems [47, 48, 49, 50, 51]. Another very used functional is the hybrid B3LYP functional [52], which combines Slater, Hartree-Fock and Becke [45] exchange with the correlation terms due to Lee, Parr and Yang [46]. This functional has shown to give results in some cases comparable to MP2 calculations, although it is prohibitively expensive in a PW scheme. When in the system are present transition metals, it has been shown that the BLYP functional fails in most cases and the Becke and Perdew (BP) functional is a better alternative [45, 53].

The majority of the studies of chemical reactivity carried out so far using DFT seem to indicate that the reaction barriers heights are generally underestimated (see for example Refs. [30, 54, 55, 56, 57]) by many of the current implementation of DFT. Proton transfer and S_N2 reactions are particularly challenging for DFT. This has been reported [58, 59, 60] to be the case for the very popular BLYP exchange and correlation functional, or its improved modification B3LYP, on the basis of a comparison with both MP2 calculations and experimental results [61, 62]. The major failure have been found in proton transfer [54, 55] and S_N2 reactions [58, 56] (exceptions exist, see, *e.g.* Ref. [63]). In many circumstances this deficiency is to be attributed to the failing of many generalized gradient functionals in describing three-centers, two-electron chemical bonds, as has been thoroughly discussed by others (see for example Ref. [64]). Therefore, in order to apply the DFT method to the studies of chemical reaction mechanisms the question of the accuracy of the calculated barrier heights is of primary importance. The validity of the functional adopted must always be controlled against more accurate approaches or the experimental data.

An additional comment is in order about the fact that current gradient-corrected density functionals are unable to describe dispersive interactions [65, 66, 67, 68], which is a key interaction for biological systems. Therefore, if van der Waals interactions are crucial in the system being studied they must be recovered in the calculation. As DFT methods include (at least partially) correlation effects in the distance range where density overlap between two interacting fragments is appreciable, the simplest way to recover dispersion interactions at long range is the introduction of empirical damped dispersion terms of the form $f(R)\ C_6R^{-6}$, where f is a damping function [69, 70, 71]. This approach has already been applied in the framework of ab initio Car-Parrinello simulations [72, 70]. More recently, in a pseudopotential calculation, it has been proposed to construct an effective potential consisting of optimized nonlocal higher angular momentum dependent terms for all of the atoms in the system in order to compensate the absence of dispersion forces in a generalized gradient approximation functional [73, 74]. This approach has given remarkably good results for many "pathological" systems [73, 75] and represents a promising method to be applied to the study of biological systems.

2.2 Hybrid quantum mechanical/molecular mechanics methods

Chemical and biochemical processes usually take place in complex heterogeneous condensed phase environments consisting of thousands of atoms. The simplest approach to overcome the limitation on the size of the system is to isolate the part of the system that is the most relevant for the function of the system itself. Usually this requires the use of geometrical constraints to impose that the original (local) structure is preserved during structural relaxation and/or dynamics. One has always to check the reliability of the model chosen enlarging systematically the system and ensuring that the results of the calculation are converged with respect to the size. This approach may require the use of very large quantum models, which include elements of the biological system not important for the function itself but that are crucial for its mechanical stability. In this scheme, long-range effects may be incorporated by including the environment electrostatic field [76] and the solvation may be taken into account by a dielectric continuum [77].

A better solution that is often used is to employ an hybrid QM/MM approach [21] in which the whole system is partitioned into a localized chemically active region, treated at quantum mechanical level, and the remaining part of the system, treated with empirical force fields. Several partitioning schemes exist [21, 78, 79, 80]. The major difficulty lies in achieving a good description of the interface region, where covalently bonds may be cut. The most common method used is the link atom approach, where the valence of QM atoms at the interface is saturated by a parameterized monovalent pseudoatom(s) or by simple hydrogen atom(s) (the so-called capping technique).

Crucial is also the treatment of the long-range electrostatic interactions. In this regard, among the possible protocols, a recent and efficient scheme is the fully Hamiltonian approach due to Rothlisberger and coworkers [79, 80, 81]. The MM subsystem is split in three regions centered on the QM part. For computational efficiency reasons, only the electrostatic interaction between the QM system and a first shell of atoms around it is explicitly taken into account. A modified Coulomb interaction is introduced in order to have the correct interaction properties and avoid an unphysical escape of electronic density to the MM atoms (the so-called spill-out effect) [79]. The electrostatic interaction between the QM region and an intermediate MM region is calculated by point charge-point charge electrostatic potential where the point charges for the atoms in the quantum region are obtained by a RESP procedure [80]. The interaction between the QM part and the more distant MM atoms are expressed in terms of multipole moments of the QM charge density and classical point charges.

The scheme due to Rothlisberger and coworkers has already been applied to many biochemical processes in the framework of the ab-initio Car-Parrinello molecular mechanics [3, 25, 26, 27, 28, 29, 30, 31]. In Section 3.2 two applications of this approach are presented [28, 3]. Other valuable QM/MM approaches are not discussed here [21].

We conclude remarking that also in a QM/MM scheme the reliability of the QM model chosen must be always checked.

2.3 Molecular dynamics

Molecular dynamics (MD) simulation based on the description of interatomic interactions via empirical force fields is a well consolidated used tool for the study of biomolecular systems. Currently, it is possible to study thousands of atoms on time scales that can reach reach the 100-ns range. Its success resides in the development of realistic force fields.

However, there are many areas in which the use of effective potentials may be not appropriate, and more sophisticated and accurate approaches are required. An alternative is offered by ab initio molecular dynamics (AIMD). AIMD in the Born-Oppheneimer approximation can be efficiently performed using the scheme proposed by Car and Parrinello (CP) [82, 83], where the electronic degrees of freedom (represented by one electron wave functions) are treated as fictitious classical variables, using a extended Lagrangian approach similar to those used in classical (with empirical force fields) MD to study thermodynamic ensembles other the the microcanonical ensemble [19, 20]. It is always possible to choose a generalized mass associated to the fictitious electronic degrees of freedom in a such a way that the latter adjust instantaneously to changes in the nuclear coordinates and the resulting dynamics is adiabatic. The method is extensively discussed in Ref. [83] (some important remarks on the effects of the fictitious electronic mass are given in Refs. [42, 84, 85]). CP MD has been intensively applied in materials science and in chemical problems. The advantage of the method lies essentially in the quality of the interatomic potential at all of the phase space points. Since the method allows an exact consideration of the anharmonic effects at finite temperature, a detailed study of the energy redistribution among the degrees of freedom as a function of time and of the polarization effects along a reaction pathway is feasible.

Limitations arising from the problems outlined in the introduction are clearly present. Given the computational cost and the space and time restrictions of using an ab initio approach it is not possible to explore the phase space of a biological system. It is necessary therefore to make hypotheses on the action mechanisms and/or structures to be considered. This is somehow a limitation in the predicting power of first principle methodologies applied to biochemical processes. As already mentioned, one successful strategy to alleviate this drawback is to couple multi-nanosecond classical molecular dynamics to AIMD. In practice the conformational space of the system is sampled via standard molecular dynamics simulations and then, on representative configurations, a AIMD/MM calculation is performed.

Finally, many chemical process involve bond breaking and forming, which often require the crossing of a relatively large activation barrier. Hence, a method to sample the relevant reaction coordinate must be employed. An huge effort has been mounted to develop sampling techniques of reaction paths in the condensed phase, as is shown by the impressive number of papers devoted to this subject [86, 87, 88, 89, 90, 91]. To date, there is not any really efficient way to explore the phase space of a reactive system in the condensed phase, which can be used routinely in ab initio simulations, that does not rely at least on an initial guess of a reaction coordinate. From a computational point of view, one of the best techniques to be applied in CPMD simulations is the *Blue Moon Ensemble* constrained molecular dynamics [91, 92], in which the system is forced to move along a suitable coordinate. Recently, multiple steering molecular dynamics [86] has also been applied in a CP framework [28, 93]. This approach allows one to work out the free-energy profile along selected reactive routes via non equilibrium MD [86]. To date, the most powerful technique to find reactive pathways is probably represented by the so-called metadynamics of hills method, which was introduced few years ago by Laio and Parrinello [87, 94]. The method is based on a coarse-grained history-dependent dynamics (metadynamics) that is able to explore the free energy in the space defined by a manifold of collective coordinates S_α that characterize the reaction process. At each metadynamics step the system evolution is guided by the combined action of the thermodynamic force (which would trap the system in the free-energy wells) and a history-dependent force, which disfavors configurations in S_α space that have already been visited. The history-dependent potential, is constructed as a sum of Gaussians centered on each value of the S_α already explored during the dynamics. This approach has been successfully applied to the study of the first steps of the oxidative damage of DNA via radical cation formation [27].

3 Applications

Because of the large number of ab initio applications to biological systems already presented in the literature, it is clearly impossible to review all of the work appeared so far. Here we report only few representative examples, which give the flavor of what it can be done nowadays exploiting the best computational resources and the state-of-the-art computational methodologies.

3.1 Electronic structure DNA

3.1.1 Electronic structure of Wet DNA

The computational study of nucleic acids and other biopolymers in laboratory-realizable conditions has until now focused mainly on their structural properties, while the nature of the electronic structure has received far less attention. Yet the electronic states play an important role in determining the interatomic forces, as they lead to electronic polarization effects and many-body forces and provide an accurate description of the dielectric properties. Furthermore, they are crucial in phenomena like radiation-induced damage [95]. More recently, there has been great interest in the nature of the electronic structure of DNA because of its potential applications to nanotechnology [96, 97, 98, 99, 100, 101]. Only recently has an effort been made to study periodically infinite double strands with high quality ab initio calculations by Gervasio *et al.* [27].

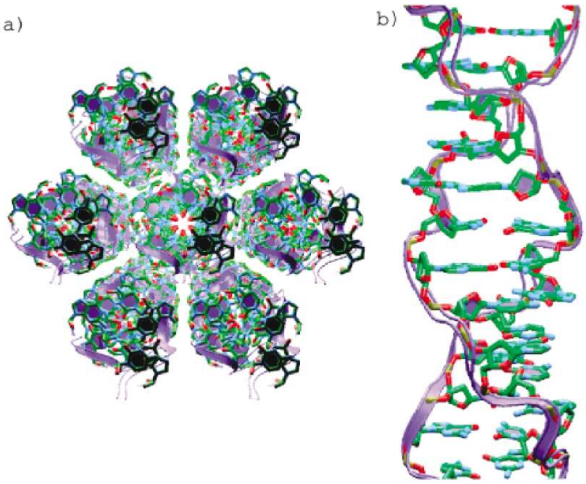

Figure 1: View of the three-dimensional structure of the G:C dodecamer [102] (a) along, (b) orthogonal to the **c** (z) axis. Water molecules, counterions and hydrogens have been removed for clarity. The sugar-phosphate backbone is represented as ribbons.

The system studied is a fully hydrated double strand self-complementary DNA (polyd(GpCp) [102], see Fig. 1). This is an infinitely repeated biopolymer, which in the unit cell contains twelve guanine:cytosine (G:C) pairs in the Z conformation. Polyd(GpCp) adopts the Z conformation only under conditions of high ionic strength and thus is rarely observed in nature. This choice, however, was made since in this particular crystal structure the DNA is continuous across crystal boundaries and because the Z conformation exhibits less thermal fluctuations than either A or B forms. [103] The system included other than the solvation water, all of the counterions, which are crucial for the stability of the DNA [104]. The model contained 654 heavy atoms and 540 hydrogen atoms. Geometry relaxation and subsequent electronic structure calculations explicitly taken into account 3,960 valence electrons (for sodium semicore states were also considered).

The calculations revealed that twelve quasi-degenerate states are positioned at the top of the valence band. These states have a π character and are mostly localized on the G nucleobases. Each individual state of this manifold is spread over several G bases (Fig. 2). The states immediately below the top of the valence band were assign to states localized also on G. The first C localized state is at 0.78 eV below the top.

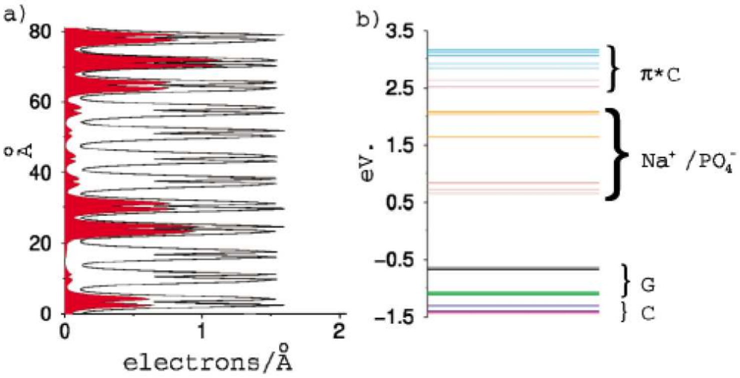

Figure 2: (a) Electronic charge density $\rho_\mathrm{e}(z)$ along the z axis integrated over the x and y directions. The integrals are performed only in regions surrounding the G basis. In red the $\rho_\mathrm{e}(z)$ of the top state is shown. The black line give the total $\rho_\mathrm{e}(z)$ of the manifold. (b) Schematic level diagram around the Fermi level. The Fermi level positioned in the middle of the gap has been chosen as the zero of energy.

The DFT gap between empty and occupied states is particularly small, being only 1.28 eV. This reflects the nature of the state at the bottom of the conduction band, which is a charge transfer state where one electron has been moved outside the helix mostly on the Na^+ counterions and on the PO_4^- groups. The effect of water molecules on this state and on the value of the gap was assessed repeating the calculation by removing the water molecules but otherwise leaving the geometry of the DNA and counterions unchanged. The gap is much reduced. This reveals the electrostatic nature of the charge transfer states and the fundamental role of water in shielding the DNA from the electrostatic field of counterions.

3.1.2 Charge localization in a DNA filament

Charge transfer in DNA is currently the subject of intense theoretical and experimental investigation [105, 106]. This is due both to a possible use of DNA as a component in nanoelectronic and electrochemical devices [107] and to the fundamental role of conductivity in the oxidative damage of DNA [27, 108]. Recent experiments have provided contradictory results, ranging from a highly conducting wire [109] and a proximity induced superconductor [110] to a semiconductor [111] or an insulator[112, 113]. Wet DNA has been shown to be a charge carrier when its length is shorter than $\simeq$ 20 Å [114]. While DNA helices longer than $\simeq$ 40 Å or in dry conditions were generally found to be insulators or high-bandgap semiconductors [115].

In a very recent study Gervasio *et al.* [18] by using fully ab initio calculations examined the effect of charge defect and the stabilization mechanism of the hole localization [116, 117, 118, 119, 120].

On the basis of this investigation, the authors excluded that in polyd(GpCp) charge localization is directly due to helix distortions. On the other hand evidence for a proton-coupled charge transfer mechanism was found. In fact, when the proton to the G:C base pair where the spin density has a maximum was

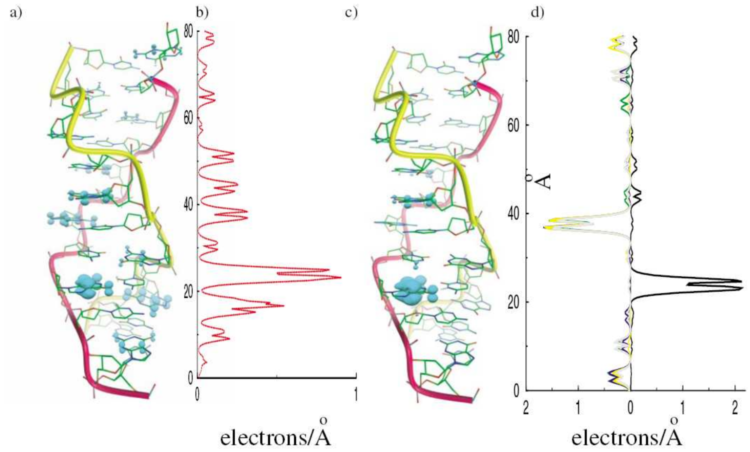

Figure 3: View of the structure of the polyd(GpCp) and of the spin density isosurface (in cyan) associated with the radical cation state a) before and c) after localization of the spin defect due to proton transfer from G to C. The isosurfaces represented have a value of 10^{-3} electrons $\mathring{A}^{-3}$. b) and d) Electronic spin density $\rho_s(z)$ projected along the z axis. b) the $\rho_s(z)$ corresponding to a). d) right, the $\rho_e(z)$ corresponding to the status depicted in c). d) left, four projections of the $\rho_e(z)$ corresponding to the shift of the proton from a different G each taken every 48 fs.

displaced, a remarkable localization of the hole on G was noticed. This lead to a situation in which the unpaired spin (the hole) is on G, yielding a $(G_{-H})^{\cdot}$ state, while H^+ moves to C, which becomes protonated (Fig. 3c and d, black line). This important result is fully consistent with a wealth of experimental data on solvated DNA [117, 119, 121].

3.2 QM/MM studies on enzymatic function

3.2.1 Ground state destabilization vs transition state stabilization

Several experimental, but somehow controversial, evidences indicate that certain enzymes can work destabilizing the ground state (GSD) of the substrate/enzyme complex [122, 123] instead of stabilizing the transition state [124], for example exerting an electrostatic or a geometrical frustration on the substrate [123]. This possibility has given rise to a long standing debate. The structure and the biological role of the few enzymes for which a ground state destabilization has been proposed are very different from each other. Therefore, to proof/disproof a ground state destabilization is necessary to analyze singularly a representative number of enzymes.

One of the enzyme taken as reference for the transition state versus ground state destabilization controversy is orotidine 5′-monophosphate decarboxylase (ODCase), which catalyzes the decarboxylation of orotidine 5′-monophosphate (Omp) to a major precursor in the formation of pyrimidine nucleotides, uridine 5′-monophosphate [122]. ODCase represents a crucial enzyme in the de-novo synthesis of DNA bases and represents one of the most proficient enzymes, enhancing the rate of spontaneous substrate decarboxylation by more than 17 orders of magnitude. Its remarkable catalytic power is entirely dependent on non-covalent binding forces and does not involve metals or other cofactors [125]. This is a very unusual characteristic among decarboxylating enzymes [122].

The remarkable proficiency of the enzyme has been suggested to be caused by GSD on the basis of X-Ray crystallography experiments [126, 127], kinetic ^{15}N and ^{13}C isotope effects [128], and free energy and binding energy calculations [126]. It is proposed that the electrostatic repulsion between the substrate and the nearby Asp70 carboxylate would drive the decarboxylation. This repulsion would be counterbalanced by the favorable binding of the phosphate tail [122, 126, 129].

On the contrary, other studies, based on EVB free energy perturbation simulations and binding energies affinities and classical MD simulations [130], invoke an ordinary transition state stabilization mechanism.

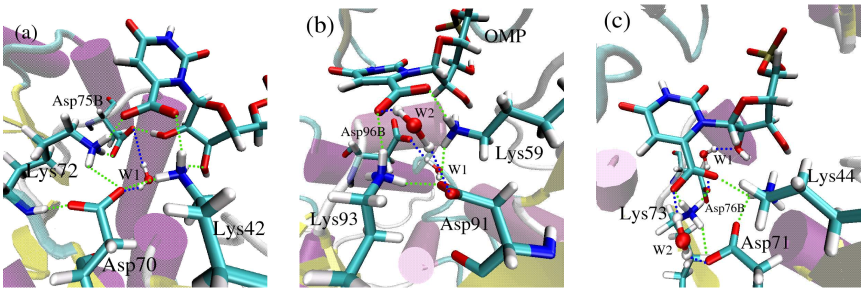

Figure 4: Snapshot of ODCase/Omp complex ground state. (a) ODCase form *Methane bacterium thermoautotrophicum*; (b) ODCase form yeast *Saccharomyces cerevisiae*; (c) ODCase form *Escherichia Coli*.

Very recently long time scale classical MD and hybrid CP/MM simulations were employed to help clarify the issue [28] The lack of structural (experimental) information on the ground state of ODCase/Omp complex was overcome by a careful construction of the model and the analysis of three different strains of the enzyme. It was found that the ODCase/substrate complex is characterized by a very stable charged network Omp-Lys-Asp-Lys-Asp, which with a direct decarboxylation driven by a ground state destabilization (Fig. 4).

On the contrary, a direct decarboxylation induced by an electrostatic stabilization of the transition state is consistent with this study. The calculated activation free energy (Fig. 5) for the direct decarboxylation with the formation of a C6 carboanionic intermediate, yields an overall rate enhancement by the enzyme ($k_{\mathrm{cat}}/k_{\mathrm{wat}} = 3.5 \cdot 10^{16}$) in agreement with experiments ($k_{\mathrm{cat}}/k_{\mathrm{wat}} = 1.7 \cdot 10^{17}$).

The decarboxylation is accompanied by the movement of a fully conserved lysine residue toward the developing negative charge at C6 position. The calculated trend of the electrostatic interaction energy suggests an extremely important role in the catalysis for Lys72, which is able to stabilize the developing negative charge at C6, and therefore the TS or, equivalently, the intermediate, and eventually provides the proton that saturates the valence of the C6 atom of Ump^-. Of course, water cannot stabilize the developing C6 charge (and therefore the intermediate) equally well.

This picture confirms also for ODCase the validity of the concept of preorganization energy [124], in which the electrostatic field generated by the enzyme active site is already organized in such a way to be complementary to the transition state charge distribution. No evidences of GSD was found as (i) the geometry of the substrate in enzyme cavity resembles very much that the most stable conformer in aqueous solution; (ii) the H-bond network accommodating the substrate is remarkably stable. In addition to Lys72 (MTBO numbering), [126, 124, 130] also Lys42 turned out to interact with carboxyl moiety of the substrate, which strongly contributes to shield the Omp carboxylate from the forming Asp70. This feature is common to all of the ODCase/Omp complexes investigated. Finally, this study clearly shows the importance of both the construction of a reliable enzyme/substrate complex and the proper sampling of the configurational space of the complex itself.

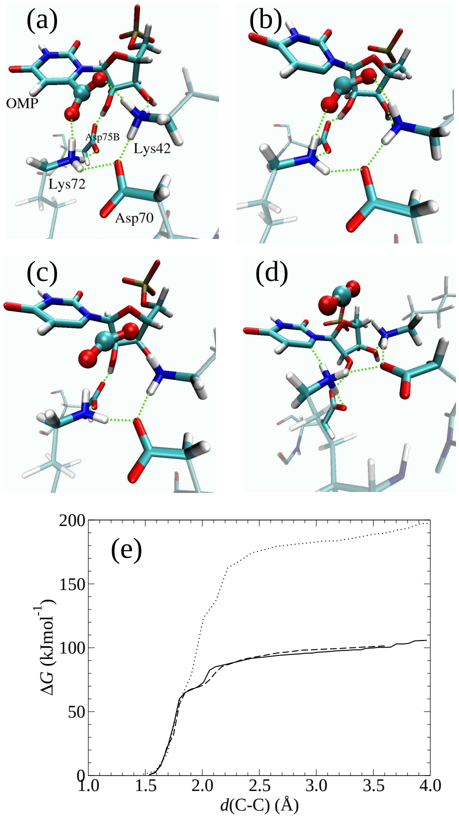

Figure 5: Decarboxylation of orotidine 5′-monophosphate. (a) Reactants; (b) breaking of the C–C bond; (c) breaking of the $CO_2 \cdots (Lys)_2$ H-bond; (d) Intermediate; (e) free energy profiles. In (e) solid and dotted lines refer to the direct decarboxylation in the enzyme cavity and in aqueous solution, respectively (the dashed line is the free energy profile calculated averaging over only one trajectory, see Ref. [28]). The residues included in the quantum sub system are evidenced: the charged network Lys-Asp-Lys-Asp and the entire substrate (Omp).

3.2.2 Photoreaction in rhodopsin

Rhodopsin proteins consist of a bundle of seven α-helices, which hold retinal chromophore in its protonated Schiff base (RPSB). The primary event in the process of vision is the absorption of a photon by the retinal. Light absorption by rhodopsin leads to conformational change in the chromophore, which is followed by a complex signal transduction pathway leading to the stimulation of the optic nerve.

The 11-cis to all-trans isomerization of the RPSB in the protein environment is ultrafast (200 fs) [131] and very efficient (quantum yield 0.65), [132] in contrast to the same photoreaction in solution. This efficiency is very intriguing because of the steric confinement of the RPSB to a small binding pocket that should hamper the large movements required to adopt an all-trans conformation. Experimental evidence reveals that bathorhodopsin, the first thermally equilibrated intermediate in the signaling cascade, exhibits a strained all-trans RPSB and stores about 134 kJ/mol of the photon energy [133].

Recently Rothlisberger and coworkers [3] have studied the conformational change of retinal on absorption of a proton with hybryd QM/MM MD methodologies, which consider the chromophore at ab-initio level, while take into account the heterogeneity and complexity of both the protein and the membrane environment by a classical force field. For the description of the first excited singlet state (S_1) the restricted open-shell Kohn-Sham (ROKS) algorithm was used [134]. This provides a good compromise between accuracy and computational efficiency.

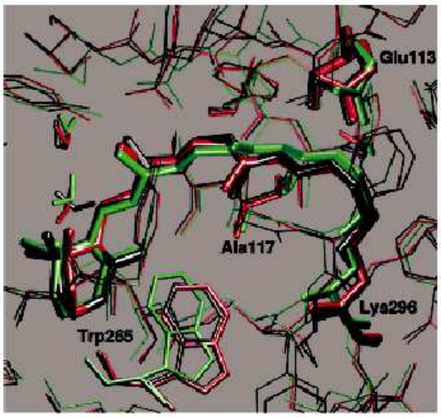

Figure 6: Superposition of the chromophore structure in the protein binding pocket in the dark state (black), at the S1 f S0 transition (red), and after 500 fs of relaxation in the isomerized state (green).

Starting from configurations sampled in a dark-state simulation, 23 excited-state QM/MM trajectories of about 100 fs each were calculated. The excited-state configuration of the RPSB is characterized by the well-known inversion of the bond length pattern. In S_1, especially the bonds C_9-C_{10} (1.44 Å), C_{11}-C_{12} (1.43 Å), and C_{13}-C_{14} (1.43 Å) are elongated, thus lowering the barrier toward isomerization. Whereas the electronic structure would be unselective toward the rotation of any of these double bonds, the protein environment favors C_{11}-C_{12} bond isomerization by steric strain. In fact, the dihedral angles from C_7 to C_{11} and from C_{12} to N deviate in S_1, similar to S_0, only by at most 15° from a perfect trans conformation. A very small barrier for the rotation around the pre-twisted dihedral angle C_{10}-C_{11}-C_{12}-C_{13} was found. This dihedral rotates to -100° and no recrossing to the dark state -35° was observed. When released to the ground state after 90 fs, the RPSB evolves toward a highly twisted all-trans structure. Remarkably, in the excited state, no atom moves more than 0.8 Å, that is, only 0.3 Åmore than the maximal thermal displacement in the dark state. After a 500 fs ground state relaxation, it was found that only the methyl groups C_{19} and C_{20} move further away from their position in the dark state. The strain is propagated through the carbon chain. The unexpected small difference between the primary photoproduct and the dark-state structure is also evident in Fig. 6.

Therefore, the 11-cis to all-trans isomerization is possible within the binding pocket with a minor atomic rearrangement, which produces a highly strained chromophore. The estimated energy stored in the system after isomerization is 117 kJ/mol, which is in good agreement with the experimentally determined energy storage in bathorhodopsin (134 kJ/mol). In the all-trans conformer, the energy stored in the internal degrees of freedom of the RPSB (+75 kJ/mol) and the van der Waals (steric) interaction energy between the RPSB and the protein (+10 kcal/mol) increase substantially, while the electrostatic interaction energy remains unaffected ($<$ 0.4 kJ/mol difference).

In conclusion, according to this study, the initial step of vision can be viewed as the compression of a molecular spring that can then release its strain by altering the protein environment in a highly specific manner.

4 Conclusions

Biological systems are particularly challenging for ab initio quantum mechanical methods. Nevertheless, first principles calculations can be used to attack problems of great current biological interest, that cannot be solved by a different approaches. In this paper we have described the state-of-the-art in ab initio (density functional theory) modeling of biological systems. This survey is clearly very limited in scope and cannot cover all of the (many) aspects of ab initio investigations of biologically relevant systems. We have tried to critically analyze the most commonly used methodologies. The most serious limitations encountered when studying a biological system are essentially (i) the accuracy to which relevant phase space regions are sampled, (ii) the degree to which the microscopic system on the computer reflects the typically macroscopic system in nature, and, in addition, (iii) the accuracy to which interaction forces are described. The first two limitations can be overcome combining ab initio calculations with more accurate sampling methodologies such as classical molecular dynamics and efficient sampling techniques of rare events. For what concern the last limitation, results must always be checked against more accurate schemes. Clearly this can be done only for model systems, which capture all the main chemical aspects of the system being studied.

Acknowledgment

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