Ψ_k Newsletter

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

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Contents

1 Editorial

In this newsletter we have three large reports on the workshops supported by the ESF Psi-k Programme. All of them contain abstracts of presented talks. A number of workshop/conference announcements can be found in the RTN2-, ESF-, and the general section advertising meetings not sponsored by either the RTN or ESF Psi-k Programme. The announcements of available positions are placed in the usual section of **General Job Announcements**. The latter is followed by the abstracts of newly submitted papers. As usual, the newsletter is finished with the scientific highlight of the month which is on **"Density Functional Studies of Molecular Magnets"** by Andrei V. Postnikov (*Yekaterinburg and Osnabrück*), Jens Kortus (*Stuttgart*), and Mark R. Pederson (*Washington DC*). The highlight is very elaborate, contains 14 colour figures and is 51 pages long. Please check the table of contents for further details.

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

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

The above contains information on the Psi-k 2004 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@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

Dzidka Szotek and Walter Temmerman
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2 News from the new RTN2

”f-electrons”

2.1 RTN2 Workshop Announcements

2.1.1 Workshop on the Electronic Structure of the Light Actinides

Riksgränsen, Sweden, May 11-16, 2004

The first workshop on the electronic structure of the light actinides will be held at the ski-resort Riksgränsen, Sweden, May 11-16 2004. The workshop will focus both on the latest theoretical developments as well as on the experimental aspects of the light actinides. The scientific program will include reviews, invited talks and contributed oral and poster presentations. There will be approximately 12-15, 1 hour invited talks and 10-15 other oral presentations, about 30 minutes long. The workshop ends with a snowmobile outing where we will drive to a lake in the mountains and there try to catch some of the Nordic Char, which we prepare for lunch over an open fire.

The location of the workshop, Riksgränsen, is an excellent ski-resort in the most northern part of Sweden where the participants can enjoy the combination of skiing, both alpine and cross-country, and midnight sun. One reaches this resort by flying to Kiruna, Sweden, where a bus will pick up all conference participants. The bus ride takes about 90 minutes.

The workshop is supported by the ESF Psi-k programme in connection with its Working Group 10 ’Psi-k f-electrons’, the EU Research Training Network ’psi-k f-electron’ and FOI, Sweden. The workshop fee, including all meals and accommodations, is 5125 Skr (570 euro) in single rooms or 4200 Skr (470 euro) in shared double rooms. The workshop fee is free for invited speakers. The scientific program, a list of invited speakers and other information will be posted at

http://www.fysik.uu.se/theomag/workshop2004

Olle Eriksson
University of Uppsala
Per Andersson
FOI
Co-chairmen

3 News from the ESF Programme

"Towards Atomistic Materials Design"

3.1 Reports on the ESF Workshops/Conferences

3.1.1 Report on the San Sebastian Workshop

Report on the Workshop

Ab-initio Electron Excitations Theory:
Towards Systems of Biological Interest

21-24 September 2003
Donostia International Physics Center, San Sebastian, Spain

http://dipc.ehu.es/arubio/dipc/bioex.html

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The aim of this Workshop was to assess the present status of theoretical approaches to the study of spectroscopic properties of real materials, and explore their capability for applications in further systems with technological and biological interest. Due to the different methods used to tackle this problem (Many-Body Theory, Density Functional Theory, Configuration Interaction, semi-empirical approaches), this Workshop was intended as a way to promote links among scientists coming from different communities working or interested in electron excited states.

The workshop was hosted by the Donostia International Physics Center (DIPC) and organized by a team of researchers belonging to four nodes of the NANOPHASE Research and Training Network. This meeting was the sixth of a series of workshops that have had an acknowledged impact in the community of scientists interested on first-principle theoretical techniques to characterize electron excitations.

Seventy seven scientists from Europe, United States, Australia, and Japan attended the workshop. The invited talks were given 30 minutes of time, and were followed by at least 10 minutes for discussion. The short contributed talks, given by young researchers, lasted 15 minutes plus five minutes (usually more) for discussion. Finally, there was a poster session with around thirty contributions. All the main authors had the opportunity to make a brief oral presentation in a special session that took place on the first day of the workshop.

Our goal was to bring together scientists working on foundations and different applications of TD-DFT and many-body theory, trying to assess the capability of current approximations to be applied to real systems of increasing complexity. The invited and contributed talks covered:

- Fundamental topics on TD-DFT, Many-Body Theory, and electron transport theory.
- New approximations and techniques.
- Ab-initio calculations of spectroscopic properties of complex materials.
- Application to biomolecular systems.

As a consequence, there was a broad variety of participants which helped to get an interdisciplinary vision of the field. Thus, although some of the more specific topics were far from the research interest of many participants, the meeting was an excellent opportunity to see how the same techniques are used by members of other communities. More importantly, the different contributions helped to show what are the bottlenecks and/or the theoretical limitations of the approaches that now are routinely used in solid-state physics to tackle problems related to biomolecular processes.

Finally, Ari Seitsonen (representing the participants interested on biological systems), and Rex Godby (from the community of solid-state scientist) closed the workshop. Appreciating the rapid development of the field, they emphasized the basic conceptual differences between the ab-initio characterization of new materials and the understanding of fundamental biological processes. They also concluded that complex biomolecules can be viewed as a challenge for those scientists working on the development of new ab-initio approaches, since they can be viewed as intermediate systems between localized (molecular) and extended (solids) systems.

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WORKSHOP PROGRAMME

SUNDAY 21

Registration and get together.

MONDAY 22

Theoretical Foundations I

09:15 Presentation and general announcements
09:30 **Eberhard K.U. Gross** (Freie-Universität, Berlin)
ELFs and Ghosts in Density Functional Theory
10:10 **Yann-Michel Niquet** (Universite Catholique de Louvain)
High-accuracy XC potentials from the linear-response Sham-Schluter equation: Asymptotic behavior and properties
10:50 Break

Theoretical Foundations II

11:20 **Francesco Sottile** (Ecole Polytechnique)
Parameter-free calculation of response functions in time-dependent density-functional theory
12:00 **Andrea Marini** (DIPC, San Sebastian)
Bound excitons in time dependent density functional theory: optical and energy–loss spectra
12:20 **Silke Biermann** (Universite Paris Sud and Ecole Polytechnique)
Electronic structure of strongly correlated materials - a view from dynamical mean field theory
13:00 Break

Biological and Organic Systems I / Posters

15:30 **Paolo Carloni** (SISSA, Trieste)
Role and perspective of ab initio molecular dynamics of biological systems
16:10 **Michael Rohlfing** (Universität Bremen)
Dynamics of electronically excited molecules
16:30 Short oral presentations of posters I
16:50 Break
17:20 Short oral presentations of posters II
17:40 Poster session

TUESDAY 23

Complex Systems I

09:30 **Giovanni Onida** (Universita di Milano)
Calculating optical spectra of surfaces and other non infinite systems using plane waves in DFT-LDA and beyond: bottlenecks and progresses

10:10 **Olle Gunnarsson** (MPI, Stuttgart)
Calculation of dynamical correlation functions:
Application to resistivity saturation

10:50 Break

Complex Systems II

11:20 **Conor Hogan** (Universitá di Roma Tor Vergata)
Electron energy loss spectroscopy at As-rich GaAs(001) surfaces

12:00 **Martin Friak** (FHI, Berlin)
Ab Initio Investigation of the Halfmetal-Metal Transition in Magnetite

12:20 **Kiril Tsemekhman** (University of Washington, Seattle)
Self-Consistent Self-Interaction Corrected DFT:
The Method and Applications to Extended and Confined Systems

12:40 **Krzystof Tatarczyk** (FHI, Berlin)
Surface Plasmons in Surface Alloys

13:00 Break

Biological and Organic Systems II

15:30 **Franz J. Himpsel** (University of Wisconsin-Madison)
Electronic Excitations at the Interface between Soft and Hard Matter

16:10 **Gero Schmidt** (Friedrich-Schiller-Universitat Jena)
Ground- and excited-state properties of small molecular systems:
Pyrimidine and purine bases in the gas phase and adsorbed on silicon

16:50 Break

Biological and Organic Systems III

17:20 **Marcus Elstner** (Padeborn Universität)
An approximate DFT approach to excited states properties

18:00 Round Table

Conference dinner

WEDNESDAY 24

Biological and Organic Systems IV

09:30 **Ari Seitsonen** (Universität Zurich)
TDDFT in molecules and extended systems

10:10 **Alberto Castro** (Universidad de Valladolid)
Investigating phenomena related to electronic excited states through time dependent density functional theory: Some examples.

10:50 Break

Biological and Organic Systems V / Electron Transport

11:20 **Marialore Sulpizi** (EPFL Lausanne)
A Hybrid Time-dependent Density Functional/ Molecular Mechanics investigation of Aminocoumarins in Solution

11:40 **Elisa Molinari** (Universita di Modena)
Optics and transport of (bio)-molecular systems: solid state effects and p-p interactions

12:20 **Arrigo Calzolari** (INFM-S3, Modena)
Electron channels in biomolecular nanowires

12:40 **Giovanni Stefanucci** (Lunds Universitat)
Different ways of treating the bias and the inclusion of many-body interactions in the description of quantum conductance

13:00 Break

Electron Transport

15:30 **Julio Gómez-Herrero** (Universidad Autonoma de Madrid)
Measuring the electrical transport properties of individual molecules: carbon nanotubes and DNA

16:10 **Peter Bokes** (University of York)
Coherent steady current-carrying states from the maximum entropy principle and the Kubo formula

16:50 **Andreas Wacker** (Technise Universität, Berlin)
Nonequilibrium Quantum Transport in Quantum Cascade Lasers

17:10 **Rex Godby** (University of York) and **Ari Seitsonen**
Concluding remarks

INVITED TALKS

ELFs and Ghosts in Density Functional Theory

E.K.U. Gross

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The lecture consists of two separate parts: In the first part, some recent developments in time-dependent density functional theory (DFT) will be presented. In particular, a time-dependent generalization of the electron localization function (ELF) will be shown. The static ELF [1] represents a tool to visualize the degree of localization of the electron distribution and, thereby, allows the classification of chemical bonds. The time-dependent version of the ELF contains an additional term arising from the phases of the time-dependent Kohn-Sham orbitals. Movies of the time-dependent ELF allow the time-resolved observation of the formation, the modulation, and the breaking of chemical bonds, and can thus provide a visual understanding of complex reactions involving the dynamics of excited electrons. We illustrate the usefulness of the time-dependent ELF by two examples: A $\pi - \pi^*$ transition induced by a laser field, and the destruction of bonds and the formation of lone-pairs in a scattering process.

Although time-dependent DFT enjoys increasing popularity as a method of calculating molecular excitation spectra [2], it often has difficulties -just like ground-state DFT- in dealing with degeneracies or near-degeneracies. To get a grip on this kind of situations we explore, in the second part of the lecture, a stationary approach to excitation energies, known as ensemble DFT. We observe that the direct Coulomb (Hartree) term appearing in the ensemble DFT for excited states contains an unphysical "ghost" interaction which has to be corrected by the ensemble exchange and correlation functional. We propose a simple additive correction to the conventional ensemble exchange energy in the form of an orbital functional. By treating this corrected exchange energy functional self-consistently within the optimized effective potential method one finds a significant improvement of atomic excitation energies [3].

[1] A.D. Becke and K.E. Edgecombe, J. Chem. Phys. 92, 5397 (1990).
[2] H. Appel, E. K. U. Gross and K. Burke, Phys. Rev. Lett. 90, 043005 (2003).
[3] N. I. Gidopoulos, P. G. Papaconstantinou and E. K. U. Gross, Phys. Rev. Lett. 88, 033003 (2002).

High-accuracy exchange-correlation potentials from the linear-response Sham-Schlüter equation: Asymptotic behavior and properties

Y. M. Niquet[1], M. Fuchs[2] and X. Gonze[2]

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There has been a recent interest in orbital- and energy-dependent exchange-correlation functionals based on many-body perturbation theory or on the adiabatic connection fluctuation-dissipation theorem. These functionals, such as the Random Phase Approximation (RPA), are indeed able to describe Van der Waals interactions for example, which are beyond the scope of the Local Density Approximation (LDA). However, the asymptotic behavior of the associated exchange-correlation potentials has remained controversial. Here we show that these potentials are in fact well-behaved, and that their asymptotic behavior reveals much physics. We discuss practical implications of these results for i) the calculation of these potentials and ii) the design of orbital and energy-dependent approximations for the exchange-correlation energy. We also discuss approximate exchange-correlation potentials, that are much simpler to compute while being likely of reasonnable accuracy.

Parameter-free calculation of response functions in time-dependent density-functional theory

Francesco Sottile, Valerio Olevano and Lucia Reining

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We have established and implemented a fully ab initio method which allows one to calculate optical absorption spectra of semiconductors and insulators, including excitonic effects, without

solving the cumbersome Bethe-Salpeter equation, but obtaining results of the same precision. This breakthrough has been achieved in the framework of time-dependent density-functional theory, using new exchange-correlation kernels f_{xc} that are free of any empirical parameter. We show that the same excitonic effects in the optical spectra can be reproduced through different f_{xc}'s, ranging from frequency-dependent ones to a static one, by varying the kernel's spatial degrees of freedom. This indicates that the key quantity is not f_{xc}, but f_{xc} combined with a response function. We present results for the optical absorption of bulk Si, SiC (exhibiting continuum exciton effects) and bulk Argon (exhibiting instead a bound exciton series) in good agreement with experiment, almost indistinguishable from those of the Bethe-Salpeter approach.

Electronic structure of strongly correlated materials - a view from dynamical mean field theory

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Dynamical mean field theory (DMFT) allows for a quantitative description of electronic correlations. Originally designed for the study of lattice models of correlated fermions, such as the Hubbard or Kondo models, DMFT has recently been combined with electronic structure techniques (DFT-LDA). This ”LDA+DMFT” approach provides a realistic description of the excitation spectra of materials with arbitrary strength of electronic correlations.
After a short introduction to DMFT, we will discuss some successes of ”LDA+DMFT”. A critical account of its shortcomings will also be given. Finally, we describe a recent attempt (”GW+DMFT”) to go beyond heuristical combinations of band structure calculations and DMFT.

Role and perspective of ab initio molecular dynamics of biological systems

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Ab initio molecular dynamics (MD) allows realistic simulations to be performed without adjustable parameters. In recent years, the technique has been used on an increasing number of applications to biochemical systems. By a survey of recent applications, we show that despite the current limitations of size and time scale, ab initio MD (and hybrid ab initio MD/MM approaches) can play an important role for the modeling of biological systems. We also provide a perspective for the advancement of methodological approaches which may be further expand the scope of ab-initio MD in biomolecular modeling.

Calculating optical spectra of surfaces and other non infinite systems using plane waves in DFT-LDA and beyond: bottlenecks and progresses

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Calculation of dynamical correlation functions: Application to resistivity saturation

O. Gunnarsson

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The calculation of dynamical correlation functions is discussed, using a determinantal finite temperature quantum Monte-Carlo method. This method is particular suited for systems with electron-phonon interaction but without electron-electron interaction, since the so-called sign problem is then absent. The method is applied to the calculation of electrical resistivity.
The resistivity of metals normally saturates if it reaches values of the order of 0.1 mΩcm. This happens when the apparent mean free path becomes comparable to the separation of the atoms, the Ioffe-Regel criterion. Several exceptions have, however, been observed, in particular High-T_c cuprates and alkali-doped fullerenes. We present models of transition metal compounds and alkali-doped fullerenes, in which noninteracting electrons are scattered by phonons. We show that the transition metal model leads to resistivity saturation [1], while the fullerene model shows no saturation [2]. Using the f-sum rule, we derive the Ioffe-Regel condition quantum mechanically [1,3]. We show that the underlying assumptions are reasonable for many transition metal compounds [1], but that they are violated for alkali-doped fullerenes [3] and High-T_c cuprates [4].

[1] M. Calandra and O. Gunnarsson, Phys. Rev. Lett. 87, 266601 (2001).
[2] O. Gunnarsson and J.E. Han, Nature 405, 1027 (2000).
[3] M. Calandra and O. Gunnarsson, Phys. Rev. B 66, 165119 (2002).
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Electron energy loss spectroscopy at As-rich GaAs(001) surfaces

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Optical spectroscopic techniques, in particular, reflectance anisotropy spectroscopy (RAS), have been used extensively in the past to characterize and understand the clean surfaces of semiconductors and metals. Increasingly, these techniques are being applied to the study of more challenging systems, such as self-assembled nanowires on surfaces, epitaxial growth processes, and even adsorbed organic molecules and proteins.

One of the early driving forces behind these techniques was the hope that well defined features in the surface layers, such as dimers, would yield useful signatures in the spectra. However, it soon became clear that this simple picture is complicated by the contribution to the optical spectra from extended states, such as surface resonances and surface perturbed bulk states. Furthermore, the signal from the surface is very weak (a relative intensity of less than 1%), making accurate measurements, and hence, comparison with theory, difficult.

An alternative surface sensitive spectroscopic technique is that of high resolution electron energy loss spectroscopy (HREELS). The shorter penetration depth of electrons, as compared with that of light, makes the technique much more sensitive to the details of the first few surface layers, resulting in measured relative difference intensities in the surface anisotropy of up to 40%. In this talk I will discuss the complementary nature of the RAS and HREELS techniques with the aid of ab initio calculations of the anion-rich GaAs(001) $\beta 2(2 \times 4)$ and $c(4 \times 4)$ reconstructions. Since calculations of HREELS spectra are usually carried out using a three-layer model which is not valid at high loss energies, or equivalently, at high transfer momentum q, the agreement with experiment is usually only qualitative. Therefore, we also consider the problem of calculating HREELS spectra beyond the three layer model, and present some preliminary results.

Surface Plasmons in Surface Alloys

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Although in time-dependent density-functional theory quantitative description of collective excitations is not yet complete, qualitative behaviour of plasmons is reproduced well even without dynamic exchange-correlation effects. In case of alkali and simple metal surfaces remarkable agreement with experiments is found already in the framework of the electron gas, allowing to believe that the accurate study of more complicated systems can be performed safetly. However, recent research done on the Al/Na, Al/K surface alloy structures puts such believes in question, since while the experimental specra show no separate plasmon excitation originating from the alloy layers, the theory clearly predicts such. This controversy provides motivation for futher studies and the testing-ground for the implementation of the method. We present the EELS and PY spectra of the above surface alloys. These have been calculated in a generalisation of the electron gas approach, in which the one dimentional ground-state potential and the density profile are obtained from the ab initio study of the real system. By comparing these findings with the jellium model calculations and the existing results by Liebsch we discuss the possible reasons for the outlined contradiction. As a side-result the usage of different exchange-correlation kernels and the density averaging schemes with their influence on the plasmon energies has also been tested.

Electronic Excitations at the Interface between Soft and Hard Matter

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The combination of organic and biological molecules with inorganic templates is becoming a vast new field with many opportunities for building up complex structures by self-assembly. This talk will focus on their electronic excitations and give an overview of the spectroscopic methods available to explore them. Among the themes will be:
1) Molecular electronics, nanotubes, switching molecules
2) Biocompatible interfaces, self-assembled monolayers
3) Block copolymer patterns

Ground- and excited-state properties of small molecular systems: Pyrimidine and purine bases in the gas phase and adsorbed on silicon

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The ground- and excited state properties of the DNA (RNA) base molecules adenine, guanine, cytosine, thymine, and uracil is not only of interest for the understanding of electron transfer processes along the DNA, but also for potential nanosize or mesoscopic devices. Due to their Watson-Crick base pairing complementarity and due to the fact that DNA molecules of specific composition ranging in length from just a few nucleotides to chains several tens of micrometers long now be routinely prepared, a wide range of promising applications of these molecules - far beyond biochemistry - are presently being explored.

We present equilibrium geometries, vibrational modes, dipole moments, ionization energies, electron affinities, and optical absorption spectra of the DNA base molecules calculated within the single-particle as well as within Delta SCF (constrained DFT) approximation. Comparison is made with results of quantum chemistry approaches and TDDFT results.

The adsorption of uracil on Si(001) is studied as an example for the interaction of a prototypical organic molecule (featuring one C=C double bond, two NH and two carbonyl groups) with a semiconductor surface. We find that the electronic properties of the uracil/Si(001) interface depend strongly on the details of the chemical bonding and adsorption symmetry. Dative-bonded interfaces are characterized by a high density of states in the energy region of the fundamental gap and a very strong reduction of the surface dipole potential, whereas covalently bonded interfaces are electronically passivated and show only small variations from the surface dipole of the clean surface.

[*] In collaboration with Martin Preuss, Patrick Hahn, Kaori Seino and Friedhelm Bechstedt

An approximate DFT approach to excited states properties

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We present an extension of our density functional based tight binding method SCC-DFTB [1] for calculating excited state energies in the framework of time dependent density functional linear response theory [2]. The SCC-DFTB method is based on a second order expansion of the DFT total energy functional with respect to a reference density, where the matrix elements are determined within a confined LCAO basis in a two-center representation. Similar approximations are applied for the calculation of excited states energies and gradients. The resulting computational efficiency of this method allows to fully relax molecular systems in excited states even for large systems or to perform extended molecular dynamics simulations. It further enables investigating all the features of potential energy surfaces as minimum energy paths, transition states and conical intersections needed for an adiabatic analysis of photochemical problems. Applications to small organic molecules and aromatic systems demonstrate the quality of our approach, reproducing the TDDFT results. However, also the shortcomings of TDDTF (GGA functionals) are inherited. We discuss some illustrative examples, like the retinal chromophore and linear polyenes, where the investigation of potential energy surfaces exhibits a qualitatively wrong description of the respective photochemistry [3].

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TDDFT in molecules and extended systems

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TDDFT has by now mainly found applications in the calculation of finite systems like molecules and clusters, due to the well-known limitations in the exchange-correlation part and possibly the formalism itself in extended systems like liquids and solids. We present a formulation of TDDFT in the plane wave basis set and within the linear response theory [J Hutter, J Chem Phys; 118 (2003) 3928]. This implementation in the CPMD code enables the calculation of excitation energies and responses to external perturbations, like forces on the atoms, dipole moment and density in the excited state. These enable calculations e.g. of adiabatic excitation energies or the electrostatic coupling in QM/MM calculaions.

We shall discuss some applications of TDDFT in molecular cases and its limitations in the extended systems.

Investigating phenomena related to electronic excited states through time dependent density functional theory: Some examples.

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Based on time-dependent density functional theory, we aim at the construction of a feasible theoretical and computational framework to investigate, from first principles, the electronic excited states (and the phenomena related to them) of large systems – up to systems of biological relevance. Attention has been placed on the optical absorption spectra, on non-linear electronic response, and on photo-induced dynamics of the systems driven on excited states energy surfaces: photodissociation, photoisomerization, etc. We will present some selected examples of our attempts, successes, failures and concerns. Systems under probe have been: the green fluorescent protein (GFP), DNA basis, the azobenzene cromophore, and some other small molecules. The computational design and techniques will also be presented.

Optics and transport of (bio)-molecular systems: solid state effects and $\pi - \pi$ interactions

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Different ways of treating the bias and the inclusion of many-body interactions in the description of quantum conductance

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A novel nonequilibrium Green's function approach is proposed in order to deal with the current response of resonant tunneling systems. Most of the previous results in this field have been obtained by using a "partitioned" scheme, i.e., the left and right lead are decoupled in the remote past and in thermal equilibrium at different chemical potentials. The current flows once an hopping term between the leads and the central quantum device is estabilished. Physically one expect that the initial correlations are washed out after very long time and hence that the steady state current should be the same as the one calculated in a "partition-free" scheme. Here the whole system is in thermal equilibrium and it is the bias rather than a contact to be switched on. Despite a more involved formulation, the partition-free approach has many appealing features being much closer to what is experimentally done. In particular, besides the static responses one can calculate physical dynamical responses too.

For non-interacting resonant tunneling system we write down an analytic result for the time-dependent current in the so called wide-band limit. We also prove a theorem of equivalence between the two schemes as far as the long time behavior of the current response is concerned. The interactions can be included perturbatively or self-consistently. In particular the non-interacting solution for the lesser Green function doesn't change at the Hartree-Fock level and this allows to study, e.g. plasmon effects, formation of dipoles at the interfaces and so on.

Measuring the electrical transport properties of individual molecules: carbon nanotubes and DNA

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In this talk we will review different experiments devoted to measure the electrical transport properties of natural DNA molecules adsorbed on a insulating subtract. The results are compared with those obtained in single walled carbon nanotubes (SWNT). The experiments can be divided in to groups:
i) Contact experiments: in these experiment a metal covered atomic force microscope (AFM) tip is used to produce a nanocontact on the molecules. Using this technique current as high as 30 mA can be obtained in the case of SWNT. The same technique does not show any evidence of electrical transport in natural DNA within our experimental sensitivity 0.1 pA.
ii) Non contact experiments: In these experiments the effects of a long range electric field is measured simultaneously in SWNT and natural DNA molecules. Again, in the case of carbon nanotubes a clear signal is obtained indicating that carbon nanotubes screen the electric field and therefore are good conductors. In the case of DNA no signal is measured indicating that natural DNA is not a conductor. This technique is independent of the particular type of contact electrodes.

Coherent steady current-carrying states from the maximum entropy principle and the Kubo formula

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In order to include electron-electron interactions in a controlled way in ab-initio calculations, we need to formulate the problem of coherent steady-state charge transport in a form different from the usual scattering-states-occupation theory, which is too closely bound to single-particle concepts. We present such an approach based on the maximum entropy principle, and discuss its advantages as well as difficulties. We discuss the results for several semi-self- consistent models for which the maximum-entropy results can be directly compared to the scattering-states approach. A further alternative, in the linear-response regime, is offered by a Kubo-like theory. We discuss the problems one needs to overcome when the electron-electron interaction is to be included, as well as some simple examples.

CONTRIBUTED TALKS

Bound excitons in time-dependent density functional theory: optical and energy-loss spectra

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Since the 30's excitons are ubiquitous in our understanding of the optics of bulk materials, surfaces, nanostructures and organic/bio–molecules. However just recently the first principle description of excitons in the optical absorption of extended systems has been achieved, by solving the Bethe-Salpeter equation of Many–Body Perturbation Theory. An alternative approach to the study of correlation in many–body systems is given by time–dependent–density–functional theory (TDDFT). In TDDFT all many-body effects are cast into the exchange-correlation kernel $f_{xc}(r,t,r';t') = \delta v_{xc}(r,t)/\delta\rho(r',t')$, where $v_{xc}(r,t)$ is the time–dependent exchange–correlation potential. However the commonly used approximation for f_{xc} based on the Local–Density Approximation (LDA) fail to describe, among other things, excitonic effects in the optical and energy–loss spectra. Furthermore, to–date, calculations of the absorption spectra of solids beyond time–dependent LDA were performed in semiconductors characterized by weak continuous excitonic effects. Consequently it remains open whether or not strong electron–hole effects (e.g. bound excitons) in the optical and energy–loss spectra can be described within TDDFT. We present a robust, efficient, frequency dependent and non–local exchange–correlation $f_{xc}(r,r';\omega)$ derived by imposing time–dependent density–functional (TDDFT) theory to reproduce the many–body diagrammatic expansion of the Bethe–Salpeter polarization function. As illustration, we show the calculated optical spectra of LiF, SiO_2 and diamond and the finite momentum transfer energy–loss spectrum of LiF. Bound–excitons as well as strongly and weakly correlated resonant excitons are well reproduced in the proposed TDDFT scheme. A favorable expression for f_{xc} is given to allow its straightforward implementation.

Dynamics of electronically excited molecules

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After excitation of its electronic subsystem, a molecule is usually no longer in mechanical equilibrium. Vibration, relaxation, and particle desorption may result. To describe this, we evaluate the geometry-dependent total energy of the system, as resulting from many-body perturbation theory of the excitation: the total energy is given by the sum of the ground-state energy (from density-functional theory) and the excitation energy. The many-body perturbation theory is evaluated within the GW approximation for the self-energy operator and for the corresponding electron-hole interaction kernel. As an example, we discuss the desorption of hydrogen from uracil which is a building block of RNA. When a low-energy electron is trapped by the molecule and incorporated in its electronic structure, the desorption of hydrogen is observed and the molecule becomes a chamically reactive radical. Such processes are supposed to contribute significantly to radiation damage.

Ab Initio Investigation of the Halfmetal-Metal Transition in Magnetite

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Magnetite, Fe_3O_4, is a ferrimagnetic material with a unique combination of interesting properties for applications in spintronics and data-storage technology. As a halfmetal, the high-temperature phase of magnetite possesses a 100% spin polarization at the Fermi surface, but its conductance is not due to majority but to minority spin electrons. Besides, it has an unusually high Curie temperature (858 K) and may be grown epitaxially using conventional deposition techniques. We present here a theoretical study of the external conditions (uniaxial and biaxial stress, pressure, substitution) that induce a halfmetal-metal transition leading to a loss of the material's desirable halfmetallic properties.

The total energies, electronic structure and magnetic moments are calculated within density-functional theory (DFT) using the full-potential linearized augmented plane-wave (FLAPW) method. Independent geometry optimizations, which take the internal degrees of freedom fully into account, show that the local-density approximation (LDA) significantly underestimates the equilibrium volume, while the generalized gradient approximation (GGA) shows excellent agreement with experimental findings. In response to uniaxial, biaxial or triaxial pressure, a halfmetal-metal transition occurs, which shifts the Fermi energy from the gap of the majority-spin electrons either under the top of the valence band or above the bottom of the conductance band, so that both spin channels become metallic. We also performed a detailed total-energy analysis of five different structural and spin configurations simulating the substitution $Fe_{2.5}X_{0.5}O_4$ (X = Mn, Co, Ni). The results allow an identification of the lowest-energy configuration in agreement with experimental observations. For Mn-substitution we find a purely metallic character, i.e., nonzero density of states at the Fermi level also for majority-spin electrons, qualitatively similar to the stress-induced transition in pure magnetite.

At about 120 K magnetite undergoes a Verwey transition, accompanied by structural deformations, whose physical nature remains as enigmatic as the microscopic properties of the low-temperature phase. It is known, however, that this transition is very sensitive to the applied stress and the impurity concentration. By treating both of these factors on the same footing and stressing their qualitatively similar effects, the presented results may shed light on the driving factors responsible for the Verwey transition.

Self-Consistent Self-Interaction Corrected DFT: The Method and Applications to Extended and Confined Systems

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We lay out a framework for the self-consistent calculation of self-interaction corrections (SIC) to the density functional theory (DFT). The technique implements the original method due to Perdew and Zunger and combines two procedures: construction of maximally localized Wannier functions (MLWF, procedure due to Marzari and Vanderbilt and to Silvestrelli) and direct minimization of the DFT+SIC total energy functional. In this formulation, the technique is applicable to both confined and extended systems. While construction of the Wannier functions is a useful tool in the case of molecules and clusters, it is a necessary step for extended systems since self-interaction energies constructed on Bloch functions vanish. Construction of Wannier functions thus provides both a good initial guess and a set of functions for which calculation of non-vanishing SIC is possible. Direct minimization scheme, similar to Car-Parrinello method, allows us to avoid solving non-trivial generalized eigenvalue problem as well as to calculate forces and structural dynamics.

We study the effect of self-interaction correction on the localization of the wavefunctions and show that, in all cases considered here, the solutions of DFT+SIC are maximally localized in space. However, in many physically interesting cases, direct minimization of the DFT+SIC functional results in the wavefunctions and density distributions that are qualitatively different from those obtained by applying MLWF procedure to LDA or GGA solutions.

In particular, contrary to the DFT result, we observe localization of spin density around a single oxygen atom near Al substitutional defect in silica and induced by this localization structural symmetry breaking leading to the significant elongation of one Al-O bond, both seen in the experiments. We also obtain several self-trapped excitons around structural distortions in silica which are lower in energy than the triplet exciton in perfect crystal. Applying SIC also stabilizes the self-trapped hole in alpha-quartz.

Because occupied and excited states are treated differently in the DFT+SIC technique, the single-particle gap in insulators and semiconductors gets significantly improved: most spectacularly, Ge is reproduced as a narrow-gap semiconductor rather than a metal predicted by the DFT. As a consequence of this effect, we get significant improvement in the formation energies of the interstitial self-diffusion in Si and Ge.

We also apply the technique to calculate the reaction energies and barriers of silane molecules. Results, although showing the correct trend with respect to the difference between the DFT (LDA or GGA) and precise all-electron calculations, appear in some cases to somewhat overcorrect the DFT results.

A Hybrid Time-dependent Density Functional/Molecular Mechanics investigation of Aminocoumarins in Solution

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Here we present a hybrid quantum mechanical /molecular mechanics approach (QM / MM) [1] to describe the optical properties of the aminocoumarins, an important group of laser dyes in the blue-green region. In the approach we use the solute (aminocoumarin) is treated at the first principle level with TDDFT [2], while the solvent is treated with a classical force field. We study the ground state and first excited singlet state properties of C151, C35 and C153, three aminocoumarins for which a homogeneous set of experimental data is available [3]. Our approach is able to quantify the effects of the chemical substituents, and in particular to reproduce the spectral redshift due to the increased alkylation at the amino position. Moreover solvation is described through a molecular approach, which permits to include in the calculations the effects due to the inhomogenities of the solvent molecules electric field. We can quantitatively reproduce the solvent spectral redshift for water and acetonitrile [4], two solvents which present a different behavior in terms of H-bond properties. Our approach is able to give quantitative information on the spectral shifts and opens the way to treatment of more complex systems, such as chromophore in a protein environment. Moreover, it can be a useful instrument for the rational design of new compounds with specific spectral properties.

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Electron channels in biomolecular nanowires

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The idea that single molecules and/or molecular arrays might be anchored to inorganic supports and integrated into electronic circuits has inspired many scientists in the last two decades. An intense research effort is being developed to identify the suitable molecular candidates, exploit them to fabricate devices, and test the device efficiency. In this paper, we discuss the advantages of employing DNA-like biomolecules to realize molecular nanodevices in which the intrinsic functionalities (e.g. self-assembly, replication, recognition) of the active component might be exploited. We focus on one particular example of a periodic molecular wire, for which an entirely first principle approach was feasible.

By means of ab-initio (plane-wave pseudopotential DFT-GGA) calculations, we investigate in detail the electronic properties of a realistic DNA-derivative (G4-wire), which consists of a quadruple helix of stacked planar hydrogen-bonded guanine tetramers stabilized by potassium metal cations.

The analysis of the electronic ground state shows that the $\pi-\pi$ coupling among stacked guanines is insufficient to induce the formation of dispersive band along the wires. However, the presence of closely spaced energy levels leads the formation of manifolds, whose density of states suggests an interpretation of the electrical properties of G4-wires in terms of effective wide-bandgap semiconductors. The actual coupling of G molecular orbitals, which may be easily induced by a weak external interaction, gives rise extended Bloch-like electron channels, suitable to host hole conduction along the wire.

Whether the formation of gathered manifolds seems to be a general feature of base-base interaction in stacked systems; the effects due to the presence of the metals depend on the specific choice of the cation. In the case of potassium, the detailed description of its electronic structure (which includes the explicit treatment of 3p semicore shell) allows us to investigate the complex metal-molecule interactions, neglected so far. With respect to the empty guanine aggregate, the inclusion of potassium enhances the conduction properties of the system generating further extended electron channels stemming from the metal-molecule interaction: The mixed sp-orbitals of K^+ hybridize with the HOMO's of guanine, and this coupling gives origin to a partially filled HOMO-derived band: G4-wire in the presence of K^+ ions acts as intrinsic p-doped system.

Nonequilibrium Quantum Transport in Quantum Cascade Lasers

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Quantum cascade lasers [1] constitute an important source of midinfrared radiation. These semiconductor heterostructure devices rely on the interplay of tunneling and optical transitions far from equilibrium, manifesting a prototype of a quantum transport device. We present transport and gain simulations of these structures using a fully self-consistent quantum mechanical approach within the theory of nonequilibrium Green functions [2]. We solve the Kadanoff-Baym equations in energy representation for the stationary nonequilibrium state using self-energies within the self-consistent Born approximation for phonon and interface roughness scattering. Furthermore the mean field potential is evaluated self-consistently with the actual carrier distribution. The gain is calculated from linear response with respect to an external infrared radiation. Starting from nominal sample parameters both the current-voltage characteristics and the gain spectrum are in good agreement with experimental findings for various samples. This demonstrates that nonequilibrium Green functions offer a strong tool for the description of modern nanostructure devices.

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POSTERS

First-principles analysis of optoelectronic properties in semiconducting polymers: The role of solid-state packing

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Ordered films of organic conjugated polymers offer an ideal scenario for the study of electronic and excitonic confinement, being composed of quasi-one-dimensional systems arranged in a three-dimensional crystalline environment. Sofar, experiments are usually interpreted in terms of a single-chain model, therefore neglecting any effect of solid-state arrangement and interchain interaction.

We investigate the effect of solid-state chain packing on both optical and transport properties for a prototype polymer, poly-para-phenylenevynilene (PPV), that is considered in different possible crystalline packings.

The optical behaviour of PPV is explored through an ab-initio scheme based on the Bethe-Salpeter equation, that allows us to include electron-hole interaction on top of a density-functional theory calculation. We find [1] that the details of crystalline arrangement dramatically alter the optical properties and lead to a richer excitonic structure: each excitonic state splits in two direct components (with electron and hole on the same chain), one for each non-translationally-invariant chain in the unit cell, and the optical inactivity of the lowest component crucially quenches the photoluminescence efficiency.

Moreover, the transport properties of PPV have been investigated [2] by converting the band-structure problem to a tight-binding formulation; this approach provides a first-principles determination of the transfer integrals, which are found to be a crucial quantity to appreciate the important effect of crystalline aggregation on conduction properties.

Our results suggest that control of interchain interaction and solid-state packing provide a tunable parameter for the design of efficient optoelectronic devices.

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Theoretical investigation of metal-modified DNA-based nanostructures

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Recent efforts in the field of molecular electronics are being extended to the use of biomolecules for device fabrication. The advantages of using biomolecules, rather than more conventional organic molecules such conducting polymers and others, are linked to their intrinc functionality (e.g., electron-transfer metalloproteins) and unique structuring. For instance, by virtue of their recognition and self-assembling properties, DNA molecules seem particularly interesting in this framework. However, whereas double-stranded DNA has been successfully employed as a template for metallic wires, its performance as a conductor is still questioned and several data indicate that native DNA attached to inorganic substrates is an insulator.

Despite this evidence, it would be very appealing to combine the structural properties of DNA with an intrinsic molecular conductivity. Therefore, ongoing investigations are devoted to the search of novel modified DNA molecules that would have suitable electronic properties. In this presentation, we focus on two possible modifications: (i) G4-DNA, which is a quadruple-helical form of DNA in which adjacent stacked planes (each plane is a guanine quartet) are intercalated by metal ions; (ii) metal insertion in double-helical DNA with controlled sequence (poly(dG)-poly(dC)). We show the results of DFT-PW91 periodic-supercell calculations of infinite G4-wires containing different metals (K, Ag, Cu) and discuss the metal-guanine hybridization and the expected consequences on charge mobility. Moreover, we show preliminary results for GC pairs in which one H-bond is substituted with a metal ion (Zn, Ag, Cu). Metal-modified DNA molecules appear as good candidates as wide-bandgap semiconductors, and the metals might behave as intrinsic dopants, either by virtue of their redox activity or because of the electronic configuration. We finally discuss the implications of our results in the framework of the ab-initio computation of I-V transport characteristics of molecular devices: the latter involve scattering properties and charge motion in molecular wires attached to metal electrodes.

QM/MM Car-Parrinello Molecular Dynamics Study of the Photoreaction in Rhodopsin

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The primary event in human vision involves the photoisomerization of the chromophore of rhodopsin, a visual pigment located in the retina. This extremely fast and efficient process is completed within 200 fs and displays a quantum yield of 0.67. Rhodopsin has been investigated thoroughly both experimentally and theoretically, but the details of the reaction mechanism and of the subsequent relaxation remain open questions. Our theoretical approach consists in the application of a hybrid classical/quantum mechanical Car-Parrinello molecular dynamics algorithm [1] that allows us to carry out excited state dynamics [2,3] for the whole chromophore, taking into account the influence of the protein environment. The model system ($\approx$ 24000 atoms) comprises the entire protein in a membrane mimetic environment composed of a water/octane mixture, while the quantum sysytem ($\approx$ 60 atoms) includes the chromophore (the 11-cis protonated Schiff-base of retinal). Our simulations yield one well-defined pathway for the isomerization, forming a highly strained all-trans retinal within the binding pocket. Classical molecular dynamics simulations give insight into the following relaxation steps on a nanosecond timescale[4].

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Cisplatin binding to DNA oligomers from hybrid Car-Parrinello/Molecular dynamics simulations

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Structure and binding of cisplatin to DNA in aqueous solution is investigated by QM/MM methodologies. In our approach, the platinated moiety is treated at the density functional level and the biomolecular frames with the AMBER force field. The calculations are based on X-ray structures of platinated DNA (in the free form, cispt-d(CCTCTG*G* TCTCC) -d(GGAGACCAGAGG)[1] and in complex with HMG protein domain A, cispt-d(CCUCTCTG*G* ACCTTCC) -d(GGAGAGACCTGGAAGG)[2] and on cisplatin docked DNA structure.
During the dynamics, the structure of the platinated DNA dodecamer rearranges significantly towards structural determinants of the solution structure as obtained by NMR spectroscopy. The calculated ^{195}Pt chemical shifts of the QM/MM structure relative to cisplatin in aqueous solution are in qualitative agreement with the experimental data. The QM/MM structure of the platinated/DNA HMG complex on the other hand remains rather similar to the X-ray structure, consistent with its relatively low flexibility.
Docking of $Pt(NH_3)_2{}^{2+}$ onto DNA in its canonical B-conformation causes a large kink and a rearrangement of DNA as experimentally observed in the platinated adducts, with NMR chemical shifts in qualitative agreement with the values in aqueous solution. Thus, the QM/MM approach presented here reveals itselv as novel and useful tool to investigate Pt/DNA adducts.

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Enzymatic mechanism of aspartic protease from first principles

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The catalytic reaction of HIV-1 Aspartic protease has recently been related to the conformational flexibility of the protein frame [1]. Here we address this issue in the context of the human

isoenzyme secretase, which features a fold other than that of the viral enzyme: whilst the latter is a 2-fold homodimer, secretase is an asymmetric monomer.
Following ref. [1], we investigate the reaction mechanism with a two-step approach. We first perform ≈20 ns classical MD. The simulation shows that substrate and protein motions are correlated. We then perform hybrid Car-Parrinello MD simulation [2] to evaluate the activation free energy of the reaction. In this approach, we adopt a quantum description (DFT/BLYP) for the cleavage site, whereas the rest of the system is described by standard force-fields. We find that,as in the viral enzyme [1], the reaction free energy is strongly modulated by the conformational fluctuations of the protein. Thus, the two different folds of aspartic proteases seem to have been evolutionary selected to features similar mechanical properties, which in turn play similar roles for the biological function.

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Optical absorption spectra of polycyclic aromatic hydrocarbons of astrophysical interest

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Polyciclic Aromatic Hydrocarbons (PAHs) are thought to be abundant in the interstellar medium and to play a crucial role for the chemistry and global energy balance in space. We present our preliminary results of the photoabsorption cross-section of anthracene ($C_{14}H_{10}$), pyrene ($C_{16}H_{10}$), coronene ($C_{24}H_{12}$) and ovalene ($C_{32}H_{14}$) in the framework of Time Dependent Density Functional Theory (TDDFT). Results obtained using two very different TDDFT implementations, namely Octopus and NWChem, are compared with available experimental results. The computed spectra are in reasonable agreement with the experimental data, especially for the low-lying excited states below the ionization potential of the species under study. Our work shows that computer codes commonly available to the community of condensed matter physicists are reliable enough for the theoretical study of the optical properties of this class of astrophysically relevant molecules. This makes them particularly precious when direct experimental data are not easily obtainable, as is often the case for the highly reactive radicals and ions of such species.

A new technique for the sp^2/sp^3 characterisation of carbon materials

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A method is devised to quantify the sp^3 fraction of an amorphous carbon sample. This method is based on the theoretical separation of the π^* and σ^* components of the carbon 1s electron energy-loss spectra. We perform density functional theory calculations [1] on graphite and a series of generated amorphous carbon structures of varying densities. The momentum transfer orientation resolved energy-loss near edge structure calculations [2] have permitted the decomposition of the K-edge of graphite into the π^* and the σ^* components. The resulting π^* spectrum is adopted and assumed to be transferable to other carbon systems pending an appropriate parametrisation of the life-time, phonon and instrumental smoothening. The method is applied to the generated amorphous carbon structures and shown to be stable over a wide range of the energy window used for spectral integration. The sp^3 fractions obtained using this method on a series of amorphous carbon structures generated using classical Monte Carlo procedure are found to be in good agreement with those obtained using the $\pi-$orbital axis vector [3] approximation. We have also applied this method on amorphous carbon samples prpared using a variety of methods and found good agreement using the functional fitting technique. From the electron energy loss calculations on the generated amorphous carbon structures, we conclude that the interchangeable use of coordination number and hybridisation state can lead to an underestimation of the sp^3 fraction of generated amorphous carbon structures especially for low and moderate density amorphous carbon.

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Electronic band structure of the C(111)2x1 and C(111):H surfaces

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The accepted model for the reconstruction of the (111) diamond surface is the (2× 1) π-Pandey chain model [1]. Nevertheless the details of its geometry, that affect the magnitude and existence of the calculated electronic gap between surface states, are still an open issue [2,3]. Converged total energy calculations [4,5,6] do not indicate either a chain buckling or a chain dimerization, with the exception of Ref.[7]. Within the DFT scheme, in absence of dimerization, this surface appears metallic while experimental data show that its electronic structure has a gap of at least 0.5eV [8]; in particular, electron-energy-loss spectroscopy [9] indicates a gap of 2eV.

We present first principles calculations of the $C(111)$ surface $(2x1)$ and of the $C(111):H$ $(1X1)$ reconstruction and electronic structure using DFT within LDA and GGA. In our calculations the clean $C(111)$ reconstructs to a π-chain without any significant dimerization or buckling. We also show our preliminary results within the many body green's function approach. Quasi-particle corrections to the surface band structure are calculated within the GW approximation.

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Excitons in carbon nanotubes: a first-principles study

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The nature of optical excitations in carbon nanotubes and their dimensionality remain an open question. On the experimental side, it is now possible to carry out optical spectroscopy on nanotubes of selected sizes and types.[1]. The results indicate that single-particle schemes are not sufficient for their interpretation. On the theoretical side, interesting phenomenological approaches were applied [2], but a realistic and quantitative calculation of the actual excitonic binding energy and spatial size requires an ab initio approach.

In this work, we present the results of our calculations of excitonic effects and optical properties of carbon nanotubes. We adopt a first-principles approach and use many-body methods such as the Bethe-Salpeter Equation (BSE), which has been used with considerable success to calculate excitonic effects in bulk semiconductors [3-5], and most recently, in one-dimensional systems, such as polymers [6]. The success of the latter reinforces the applicability of the BSE to one-dimensional systems such as nanotubes. The novelty of our approach consists in the symmetry analysis of the nanotube in which we take advantage of the invariance of the tube with respect to screw-symmetry operations. Such an analysis not only reduces the computation effort required, but also offers a better understanding of the physics involved, including the nature of the excitons and of the optical transitions. We show final results for the optical spectra, exciton binding energy and wavefunctions for selected nanotubes, and use them to discuss trends in exciton dimensionality as a function of nanotube size and geometry.

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Dielectric response of graphite and carbon nanotubes

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The dielectric response functions of graphite and of small-diameter carbon nanotubes (4 Å) of three different helicities were determined within the random-phase and adiabatic local density approximations.
Our findings outline the important anisotropy in the dielectric response, both in the optical and electron energy loss spectra, as evidenced by the existing experimental observations.
More specifically the local field effects in the response are significant for certain polarizations of the applied perturbation. Similarly, the interlayer (for the case of graphite) and inter-tube interactions have a strong effect on the loss function, in particular in the range of the higher-frequency $\pi + \sigma$ plasmon. We also discuss which aspects of the dielectric response of the tubes can be explained from the response of the graphene sheet which is the common structural block for both graphite and the tubes.

GW Total Energies from the Space-Time Supercell Code

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We present converged first results resulting from the incorporation of self-consistency and *GW* total-energy techniques into our general-purpose "space-time" supercell code suite [1,2], which interfaces with pseudopotential plane-wave DFT calculations as its input. This allows the extension of the *GW* total-energy approach from high-symmetry test systems [e.g. 3,4] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the ususal DFT-based approaches, including the delicate energy barriers important in biological problems.
We present results for bulk silicon, and other systems, at three levels of self-consistency: G_0W_0 (the normal non-self-consistent calculation), semi-self-consistent GW_0, and fully self-consistent *GW* (the last two approximations being particle-number conserving).

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GW alculations for Spherically Symmetric Systems

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We present details of two different studies of the GW approximation applied to systems with spherical symmetry for calculating ground-state and excited-state propertries.
First, we present an investigation into the applicability of the pseudopotential approximation within GW using the test case of an isolated closed shell atom. The quasiparticle spectrum, especially the Ionization Potential (IP), is calculated for an all-electron atom and a pseudo atom. It is found that the psudopotential approximation does not damage the agreement with experiment, contrary to suggestions by Ku and Eguiluz [1]. Also studied is the effect of partial and full self-consistency on the IP.
The second investigation is a study of the ground state total energy of Jellium Spheres using the Galitskii-Migdal formula with none, partial and full self-consistency in the GW approximation. These types of calculations have been very successful for systems with high symmetry [2,3,4]. We are now investigating the applicability to finite sized systems. Jellium spheres are an ideal prototype system since the importance of correlation can be tuned by varying two parameters — the Wigner radius, r_s, and the number of electrons.

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Short range correlation effects in the van der Waals interaction between jellium slabs

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The RPA treatment of the correlation energy in many electron systems fail to describe the short range correlation effects. Thus, the evaluation of the ground state correlation energies of electron systems either for extended or finite systems within the RPA usually overestimate the actual energy. However, when we are interested in the energy differences the RPA seem to reproduce accurate results in some cases thanks to the cancellation of it's inherent errors. This is the case in the evaluation of atomization energies or jellium sphere surface energies. Similar cancellations have been reported for the evaluation of surface energies and van der Waals (vdW) effects in jellium slabs. Our aim in this work is to make a closer and more complete study of the case, where partial RPA error cancellations are present, taking into consideration non local short range correlation effects. The exchange correlation kernel, f_{xc}, defined in the context of time dependent density functional theory (TDDFT) contains all the effects beyond the RPA level. A practical way of obtaining this kernel is to adapt those of the homogeneous electron gas (HEG) for the inhomogeneous case through different functional approximations.

The short range correlation effect on the van der Waals interaction between jellium slabs appear most significantly at small separation and intermediate distances where the electron density overlap is significant, while the behavior at large separations is properly accounted for within the RPA. In previous studies by Dobson and Wang only strictly local kernels had been considered. We have considered in addition a nonlocal $q_{||}$ dependent Hubbard like kernel.

We have extended these studies to the case of three jellium slabs in order to see how van der Waals (vdW) correlation energies are added. Also an example model system is considered in order to study how sensitive is the equilibrium bonding distance to different choices of the kernel.

Realistic investigations of correlated electron systems with LDA+DMFT

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In the last few years, the merger of conventional band structure theory in the local density approximation (LDA) with the many-body dynamical mean-field theory (DMFT) has been proven to be a powerful tool for the realistic modeling of strongly correlated electron systems. This talk provides a brief introduction to this novel computational technique and presents the results for two prime examples of strongly correlated electron systems, i.e., the magnetic and orbital properties of 3*d* heavy fermion system LiV_2O_4 and explanation of the similarity of the experimental photoemission spectra of $SrVO_3$ and $CaVO_3$.

Non-Equilibrium Electronic Occupations from the Maximum Entropy Approach

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We present calculations of non-equilibrium electronic occupancies as predicted from a Maximum Entropy Theory (MET) for simple model resonant tunnelling structures. Contrary to the traditional approach, in which left- and right-going states are occupied up to two different electro-chemical potentials, in the MET the ability of a state to carry the current influences its occupation. This results in shifts and distortions of the Fermi sphere as the system is driven out of equilibrium. As a result, for systems where the transmission coefficient varies rapidly with energy, a gap opens in k space. I-V characteristics as predicted by the MET for our model system are presented and discussed. As a result of the steady-state constraint imposed on the Hamiltonian in our approach coherent linear combinations of left- and right-going states are predicted. The existence of these in real systems is discussed, and their effect on the I-V characteristics is examined.

The ab initio electron energy loss spectra of the cubic, tetragonal and monoclinic phases of ZrO2 zirconia

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The electron energy loss spectrum (EELS) provides informations about the chemical and crystallographic environment, and the electronic structure of a crystal. We present results of an ab initio study of the electronic properties and of the EELS spectrum of the various phases of pure ZrO2, in which the local coordination of the transition metal atom evolves from Z=8 (cubic and tetragonal phases) to Z=7 (monoclinic phase) and to Z=6 in the hypothetical rutile phase. We study the influence of the local environment on the valence plasmon at 15 eV, on the collective excitation at 25 eV coming from the linear increase of the real part of the dielectric function, and the simultaneous decrease of its imaginary part, and on the plasmon resulting from the excitation of the 4p electrons at 43 eV.

Ground and Excited States of Cu_2O

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Cuprous oxide has been extensively studied during the last decades, mainly because of its exciton series in the optical range. Cu_2O is a good starting point to address the fundamental issue of transition metal oxides. Indeed, this material has a cubic structure, a closed d shell, and is non-magnetic. The topic of transition metal oxides is now very important: it is known that density functionnal theory fails to predict a gap in various insulating oxides like CoO, CuO, Ti_2O_3.

We performed DFT and GW calculations using a plane-wave basis set and the pseudopotential technique. We carefully studied the role of semicore states ($3s^2 3p^6$). Though deep in energy, these states have a large overlap with valence bands. Their influence is drastic on structural properties, but slight on the Kohn-Sham band structure. We show that the semicore states have to be included in the GW calculation to get meaningful results.

Theoretical Study of the Doped Titanium Oxide

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Many researches about photocatalytic system of titanium oxide has been carried out. However, this photocatalytic system work only under ultraviolet light (<400nm), which exceeds the band-gap energy of 3.0ev in the rutile crystalline form of TiO2. In other words, we can use very little quantity of light in our life space. Recently, it is said that nitrogen doping of TiO2 gives photocatalytic system to TiO2 under visible light (<500nm). We investigated the structure, the cause of photocatalytic system about nitrogen doped TiO2 in terms of the band-gap.

Formation energies of native defects and Zn impurities in GaP

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Zn is a well known p-dopant in various III-V semiconductors. The diffusion of Zn in GaP has been studied experimentally [1] and here we present a theoretical investigation of the experimentally proposed diffusion mechanisms. Defect eigenenergies, electronic and atomic structures, defect formation energies and charge transfer levels have been calculated for both substitutional and instertitial Zn impurities as well as for all native defects.

The computations have been performed using ultrasof Vanderbilt pseudopotentials within the VASP DFT-LDA code.

All properties have been calculated under stiochometric conditions in a supercell geometry with fully relaxed defects. We conclude from the different diffusion mechanisms and from the defect concentrations that the kick-out mechanim should be the favoured diffiusion mechanism. In addition comparisons have been made with similar defects in InP [2].

The formation energy and charge transfer level dependence of the supercell size was also studied as a means to minimize the spurious defect-defect interaction.

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Electron-hole excitations in 3*d* transition metals: IXS and ab initio calculations

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We report an all electron study of the dynamical structure factor S(q, ω) of 3d transition metals. The response is calculated in the framework of time-dependent density-functional theory

(TDDFT) based on an LAPW ground state with local-density approximation (LDA). We find that for low energy and large momentum transfers electron-hole excitations involving electrons from the narrow d-bands above and below the Fermi level can be directly identified on the energy loss spectrum. Our calculations agree very well with inelastic X-ray scattering (IXS) measurements and illustrate the potential of this technique for the investigation of the electronic structure of correlated materials.

Optical Properties of Germanium-Silicon Alloys

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In the present paper we present preliminary results on the linear optical properties of Si-Ge alloys [1]. The Si-Ge alloy system has been simulated by a set of (positionally ordered) crystals where Ge and Si atoms are distributed in different ways into diamond-like lattice sites [2]. Optical absorption spectra have been determined within the DFT-LDA-RPA approximation as function of the composition of the alloy. Present results have been compared with available experimental data and other theoretical results [2,3].

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Structural relaxation effects on the electronic excitations and optical properties of Ge nanocrystals embedded in a SiC matrix

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We propose a combined method to efficiently perform ground- and excited-state calculations for relaxed geometries using both a first-principles approach and a classical molecular-dynamics scheme. We apply this method to calculate the ground state, the optical properties, and the electronic excitations of Ge nanoparticles embedded in a SiC matrix. Classical dynamics is used to relax the large cell system. First-principles techniques are then used to calculate the electronic structure and, in turn, the electronic excitations and optical properties. The proposed procedure is tested with data resulting from a full first-principles scheme. Good qualitative accordance has been found between the results after the two computational paths regarding the structure, the optical properties and even the electronic excitations.

Quasiparticle band structures and optical spectra of β-cristobalite SiO_2

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The organic functionalization of semiconductor materials, in particular Si,and their compatibility with biomaterials have been investigated more intensively in the last years. Used as insulator in silicon devices, SiO_2 also needs to be investigated in more detail, concerning its electronic and optical properties. Keeping this aspect in mind, we present calculations of quasiparticle band structures and dielectric functions for β-cristobalite SiO_2 calculated using density functional theory and local density approximation. We apply a plane-wave code in which interaction between valence electrons and nuclei are described by pseudopotentials generated in accordance to the Projector Augmented Wave method. Three variations of the space-group symmetry for this SiO_2 polymorph are considered: Fd3m (ideal *fcc*), I$\bar{4}$2d (tetragonal),and P$2_1$3 (simple cubic). Because β-cristobalite SiO_2 is structurally simple, it is suitable to the theoretical modelling of the silicon/oxide interfaces. Quasiparticle shifts are calculated within a GW approach which describes the inverse of the dielectric function by a model function depending on the local electron density. We compare the band structures and dielectric functions calculated in both independent-particle and independent-quasiparticle picture with the available experimental data and previous calculations.

Effects of oxidation on silicon nanocrystallites

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Biocompatibility of semiconductor materials is a desirable feature for the development of biosensors, in particular optical sensors. The luminescence observed in porous silicon (p-Si) is known to be related to nanostructures formed on the surface of this material. The real mechanism that makes feasible the radiative recombination is still controversial. On the other hand, there is experimental observation that confirms the relationship between optical properties and oxidation of p-Si. Spherical-like silicon nanocrystallites (NCs) have attracted special attention, since the optical activity in p-Si can be also related to confinement effects. Several investigations have focused on the influence of surface passivation on Si NCs by hydrogen, hydroxyl group and silicon-oxygen double bond terminations. However, a more realistic model for the oxidation, including more SiO_2 covering shells on the NCs has not been considered so far. We apply a plane-wave code which makes use of pseudopotentials generated in accordance to the Projector Augmented Wave method to study the influence of oxidation in the structural and electronic properties of Si NCs. The atomic positions are optimized under T_d symmetry in order to obtain vanishing forces on the atoms. Effects of passivation and oxidation in Si NCs are discussed, concerning the relaxed structures, the resulting confining potentials of the NCs, electronic levels, localization of the HOMO and LUMO states, pair excitation energies calculated by the ΔSCF method, and oscillator strengths.

First principles calculations of optical properties in systems involving Si-O bonds

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SiO_2 is one of the most fundamentals oxide systems, in terms of structure and bonding. Materials involving Si-O bonding have a wide application in electronic industry. Recently, the strong interest in achieving further progress in microscopic-scale device fabrication raised the importance of understanding the atomistic mechanisms of Si(100) surface oxidation [1].
¿From the theoretical point of view, it is important to have a full control of the effects due to physical approximations, separating them from those related to numerical convergence issues. This is essential in order to be able to obtain reliable (and quantitatively predictive) theoretical spectra for realistic structures. For this reason, our study starts with an accurate determination of the bulk SiO_2-α absorption spectrum in the 0th order approximation to QP energies, using DFT-LDA and norm-conserving pseudopotentials. We analyze all convergence properties with respect to the number of bands, the energy cutoff, and -most important- the Brillouin zone sampling [2]. In view of our ongoing calculations for systems involving Si-O bonds, we also present preliminary results (neglecting excitons) for an oxidized Si(100) surface and for different isomers of Si_nH_mO clusters, taking into account the effects of a full structural relaxation.

Indium Quantum Chains on Silicon(111) Surface

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The structural, electronic and vibrational properties of interesting and frequently studied indium-induced (4×1) and (4×2) surface reconstructions on silicon(111) are investigated with the purpose of finding the most agreeable with respect to the experimental data obtained for structural and spectral properties. The calculations are performed using density functional theory in the generalized-gradient approximation and ultrasoft pseudopotentials. The surfaces are modeled by repeated slabs of 6 bilayers of silicon, adlayers of Si and In and a vacuum region with a thickness of 6 bilayers. The back surface of the slab is hydrogen terminated. Reconstructions with 0.5 monolayer (ML), 1 ML and 0.75 ML indium coverage of the silicon substrate are analysed by comparing the formation energies of the systems. From the corresponding phase diagram the energetically most favourable geometry is derived. It is consistent with experimental data and close to the reconstruction suggested by Kleinman et. al. The (4×1) reconstruction consists of a zigzag rows of silicon atoms and two zigzag rows of indium atoms. The (4×2) structure is just a slightly distorted modification of the (4×1) structure. Both reconstructions clearly exhibit a metallic character. For the (4×1) structure phonon frequencies at the Γ point are derived from the force-constant matrix, obtained by computing all Hellmann-Feynmann forces after displacing each atom in each possible direction 0.01Åaway from its equlibrium position. 14 atoms in the system are taken into consideration: 4 indium atoms and 2 additional silicon atoms at the surface, and 8 silicon atoms of the sublayer. It is found, that in the low-frequency region vibrational modes are mainly related to In-In bonds since the In atoms are heavier than silicon atoms. Frequencies obtained from our calculations are very close to values measured with Raman spectroscopy.

Different ordering of surface dimers and their influence on the band structure of Si(100)

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Accurate ab initio calculations using density-functional theory [1] and quantum Monte-Carlo methods [2] have identified buckled dimers as the principal element of the reconstruction of the Si(100) surface. In addition, the interaction of neighbouring dimers leads to a long-range order of the buckling directions, but the precise orientation of the dimers at different temperatures is difficult to observe directly due to thermal averaging effects in scanning tunneling microscopy and still requires further careful investigation.

One possible way to determine the actual ordering of the dimers is the comparison of angle-resolved photoemission or two-photon photoemission data with theoretical band structures, because the electronic excitation spectrum depends sensitively on the surface geometry. Therefore, we derive directly comparable ab initio quasiparticle band structures for various reconstructions of the Si(100) surface and analyse how the different orientation of the buckled dimers changes the band structure.

In contrast to earlier work at the level of the local-density approximation [3], we calculate the quasiparticle band structure by performing self-energy calculations within the *GW* approximation, using the space-time approach [4]. Noting the surprisingly large influence of spurious polarization effects between neighbouring supercells in cluster calculations [5], we devote special attention to the convergence of the quasiparticle energies with respect to the vacuum spacing in our periodic slab arrangement, a factor that has not been studied explicitly in previous *GW* calculations for surfaces. Starting from the (2×1) reconstruction, where all dimers are aligned in the same direction, we compare the band structure with that of the p(2×2) reconstruction, where dimers in the same row are alternatingly buckled. We also consider the c(4×2) reconstruction, where alternations in the dimer orientations are extended to neighbouring rows. By folding the band structures of the three different surface unit cells into the same Brillouin zone, we can directly identify the effect of changes in the dimer orientations.

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Assessment of competing mechanisms of the abstraction of hydrogen from CH_4 on Li/MgO(001)

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First-principles calculations based on the DFT-pseudopotential method with plane wave basis sets are used to study the energetics of H abstraction from CH_4 on the Li-doped MgO(001) surface. Experimental work has led to the proposal of two competing mechanisms for the reaction: either direct interaction of CH_4 with an O^- hole state bound to the Li dopant, or interaction of CH_4 with a surface F centre whose charge state is modified by the presence of the dopant. The calculations are performed in periodically repeated slab geometry, with attention given to system-size errors. For direct interaction with the hole state, the calculations indicate that the reaction is weakly endothermic, by about 0.2eV, but for the F-centre mechanism it is endothermic by over 1eV. Even allowing for likely DFT errors of a few tenths of an electron volt, this gives strong evidence against the F-centre mechanism.

Ab-initio calculation of sulfur- and carbon-based molecules on Cu(100) surface

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Using DFT-LDA ab initio calculations, we investigate the electronic properties of sulfur dioxide and carbon monoxide [1] on the Cu(100) surface, with 0.25 ML coverage. In a number of organic adsorbates on Cu and Au surfaces (e.g. methanethiolate, thiols, thiophenes), sulfur is adsorbed directly on the metallic surface, acting as a hook for the whole molecule [2][3].

We present results for the electronic density of states (DOS) of the above systems. In the case of sulfur dioxide, we also compare the DOS with that of the single S atom on Cu(100) and with the photoemission results of [3], to support the idea of S being the hook of the molecule.

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Theoretical study on molecular excitation using chirped pulses in the condensed phase

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In this Letter, a theoretical analysis shows that for complete population inversion, the adiabatic population inversion due to chirp (APIC) has much the same time evolution as adiabatic inversion. We show that APIC is caused by a long frequency sweep in place of an infinitesimal interaction, and is more important than the positive chirp effect. We also show that arbitrary pulse durations can be selected if a suitable Rabi frequency, i.e., the laser intensity, and chirp rate are chosen. This conclusion mean that APIC is a very effective method in the case when a system has ultrafast relaxation.

3.1.2 Report on the 13th Sardinia Workshop

Report on the XIII Workshop on Computational Materials Science held from 13 to 18 September 2003 in Geremeas (Cagliari), Sardinia, Italy

The thirteenth edition of the Workshop on Computational Materials Science [formerly known as Computational Condensed Matter (1990-1994) Italian-Swiss (1990-1997) Workshop] was held on the south-eastern coast of Sardinia, Italy from 13 to 18 September. The main sponsors were the Sardinia Region, the University of Cagliari, and the Ψ_k European Science Foundation Program; UNESCO bestowed its prestigious patronage. Nearly 70 participants gathered at the Workshop, in the pleasant framework of the Calaserena Village sea resort, in an informal atmosphere. As customary in this workshop, social and scientific programs blended together nicely (a two-evening poster session was the highlight) favoring intense discussion and contacts. Three sessions of the program were devoted to contribution sessions, especially from young scientists. The chance of presenting their own work to an expert but informal audience has been very much appreciated.

The traditional focus of this workshop is ab initio electronic structure, mostly within density-functional theory. Tight binding and ab initio molecular dynamics, as well as less-common topics such as polarization theory have been well represented in past editions. While keeping with the tradition of past meetings, this workshop has devoted some attention to semiempirical and model approaches, to statistical mechanics, biophysics, biological modelling, and experiment. This implies (given the sum rule on the workshop length) that the cross section of each single topic is somewhat smaller than usual, but this program formula had the definite merit of opening up new perspectives and contacts in the form of new or unfamiliar viewpoints, besides the obviously necessary confrontation with inputs from experiment. A somewhat arbitrary classification of the 17 one-hour invited talks shows that there were 5 ab initio ones, 5 on statistical mechanics-related topics, 2 on semiempirical, classical, and analytical methods, 2 on biophysics and biological modelling, and 3 on experiments.

One of the ab initio studies focused on the extensions of DFT to the treatment of excited states, such as TDDFT and GW (Lucia Reining), while the talk of Alfredo Pasquarello reviewed the state of the art on the calculations of infrared and Raman spectra of disordered oxides. The first contribution of Carla Molteni was devoted to the surface properties of liquid metals with a particular attention to aspect of layering. The second talk of Carla Molteni gave an overview on results on semiconductor nanocrystals within the framework of ab initio calculations. The two lectures of Michele Parrinello described the strategies to bridge time scales during simulations of relevant processes, as the ones occurring during structural phase transitions and in biological systems. Biological systems were the subject of the first talk of Elisa Molinari, who discussed the importance of electron transport. Elisa Molinari continued the overview of aspects connected to the transport related to organic semiconductors during her second lecture. Dietrich Wolf presented results on heteroepitaxy stressing the aspects related to the interfacial mixing. Empirical methods have been employed in the study of smetic liquid crystals, whose properties were described in the interesting talk of Claire Loison. An alternative view of *first principles* has been presented in the lively overviews given by Ellad Tadmor, who introduced concepts and applications of the Multiple-Scale Modeling to mechanical problems. Finally, methods from statistical mechanics have been described by Davide Marenduzzo for the study of liquid crystals with an overview on technologically relevant applications. Experimental works have been reviewed by Jan Peter Toennies and Franz Himpsel with very clear and appreciated lectures. Himpsel has presented a large variety of surface phenomena related to the decreasing dimensionality of the systems, while Toennies's talks have shown the wonderful and intriguing world of helium clusters with relevant connections to superfluidity.

Contributed talks (9) gave to young scientists the opportunity of presenting their results on new methods, on surface physics, on the action of antibiotics, on structural properties, on phase transitions, on superconductors, as well as on the problem of the Schottky barrier and on recent improvements on TDDFT. The range of topics mirrored the spectrum of the invited talks. The over 20 posters presented in two lively evening sessions focused mostly on ab initio (with some semiempirical tight binding blend) simulations. Among the topics touched upon, let us mention ab initio study of clusters in astrophysically relevant conditions, metal and semiconductor surface dynamics, quantum structures, electronic structure of nanowires, optical properties, nanostructures, accelerated methods to study long-time-scale phenomena etc.

The available abstracts of the lectures and the list of contributed talks posters follow below.

INVITED TALKS

One-dimensional atom chains at surfaces

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In recent years it has become possible to realize atomic chain structures on silicon surfaces that come rather close to the ideal one-dimensional solid. Electrons near the Fermi level are de-coupled from the substrate because there energy lies in the band gap. The metal atoms, however, are rigidly tied to the silicon lattice in substitutional positions according to first principles band calculations x-ray diffraction. That makes a Peierls transition to an insulator unfavorable and creates an opportunity for observing exotic states predicted for one-dimensional metallic electrons. Most strikingly, the hole left behind after exciting an electron is predicted to decompose into two collective excitations in one dimension, one with spin character (spinon), the other with charge character (holon). Such atom chains are characterized by scanning tunneling microscopy and angle-resolved photoemission. The resulting energy bands and Fermi surfaces can be tuned between 2D and 1D by increasing the chain spacing, with the intra-chain / inter-chain coupling ratio varying from 10:1 to 70:1. Unexpected metallic bands are found, such as a pair of nearly degenerate, half-filled bands, a quarter-filled band, and a fractional electron count of 8/3 electrons per 1x1 cell.

Thermal Fluctuations and Punctual Defects in a Smectic Liquid Crystal, a Molecular Dynamics Study

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We investigate the lamellar phase L_α built by amphiphilic molecules in aqueous solutions. This liquid crystalline phase (smectic) is used as a solvent for polymers to synthesize new complex materials (*e.g.* DNA + cationic lipids complexes). The instability of some polymer-L_α complexes is attributed to the influence of the polymer on the elasticity and the defects of the smectic. The aim of the study is to describe the insertion of a linear polymer between the bilayers of the smectic at both the molecular and the mesoscopic length-scales.

To compare L_α phase with and without polymer, we perform molecular dynamics simulations of a stack of amphiphilic bilayers which are planar (on average), parallel to each other, and separated by layers of solvent. The idealized, coarse-grained model represents the solvent with soft spheres, the amphiphiles with tetramers (two solvophilic spheres and two solvophobic spheres) and the polymer with bead-and-spring chains. Two polymer-types were simulated: adsorbing or non-adsorbing on the bilayers.

The position fluctuations of the simulated bilayers are well described by the "Discrete Harmonic"-theory of smectic elasticity, so that the two elastic constants -the bending rigidity K_c and the smectic compressibility modulus B- can be computed. We observe that the interactions between the bilayers are softened in the presence of a polymer (adsorbing or non-adsorbing).

Additionally, the influence of the polymer on the pores was studied. It turns out that transient pores spontaneously nucleate in the bilayers of the simulated lamellar phase even without the polymer. The size and shape distributions of these pores are investigated. The presence of a non-adsorbing polymer triggers pores in its surroundings, whereas the adsorbing polymer has no notable influence on these point defects.

Lattice Boltzmann simulations of liquid crystal hydrodynamics: applications to rheology and devices

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The hydrodynamics of liquid crystals can be described by the Beris-Edwards model, which couples a differential equation for a tensor field describing the orientational order of the molecules to a Navier-Stokes equations determining the velocity field of the fluid. A full numerical solution of these equations is very rare due to the complexity of the problem and severe approximations are routinely made.

Here we describe a lattice Boltzmann algorithm suitable to this task. No approximations apart from discretization are in principle involved. In particular viscoelastic effects and backflow (i. e. the back effect of the director field distribution on the liquid crystal fluid velocity) are fully considered. Backflow in particular is known in simple cases to heavily impinge on rheological properties of viscoelastic fluids and on the switching properties of modern liquid crystal devices. Well-known examples are respectively shear-banding in polymeric liquid crystals and the optical bounce during the switching off of twisted nematic devices employed e.g. in laptops.

We first report results of lattice Boltzmann simulations of hydrodynamical rheological properties (shear and Poiseuille flow) in a) a nematic liquid crystal when there are elastic distortions imposed e.g. by conflicting anchoring to the boundaries and b) a cholesteric liquid crystal. The situation in a) is of concern to modern device builders (e.g. for the characterization of the so called HAN cell), while that in b) stirred considerable interest in the past due to puzzling experimental measurements. We discuss the implications of our results to these topics. Then, we show the potential to apply our simulations to present-day devices. In particular we consider nematic devices where the boundaries are chemically treated so as to induce a non-homogeneous anchoring. The electric field-induced switching dynamics in these modern devices is shown to be completely changed if backflow is included in the simulations, thus pointing to the importance of a detailed treatment in order to fully exploit the device possibilities.

Electron states and conduction of biomolecules

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Abstract not available

Optics and transport of organic semiconductors

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Abstract not available

Layering at liquid metal surfaces

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Liquid metal surfaces play an important role in many technological processes.

At variance from dielectric liquid surfaces, metallic liquid surfaces stratify in layers, due to the strong interplay between atomic structure and conduction electrons. This layering phenomenon for free surfaces has only recently been observed experimentally by x-rays reflectivity measurements in Ga, Hg and In; very recent measurements have also been made for K, but layering in alkaline metals is difficult to observe experimentally because of their large thermally induced surface roughness, resulting from their low surface tension. Still alkaline metals are very interesting to study because their conduction electrons are nearly free, in contrast to other metals such as Ga with a tendency toward covalent bonding.

To complement and help elucidating the experimental data and the surface layering mechanisms, we have performed extensive first principles molecular dynamics simulation for liquid surfaces of Na, chosen to represent the alkaline metals, at different temperatures. The interplay of atomic and electronic structures has been analyzed in details.

Semiconductor nanocrystals by first principles molecular dynamics.

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Nanocrystals are playing an increasingly important role in solid state physics, chemistry, materials science, and even biology and medicine. Many fundamental crystal properties (e.g. melting point and band gap) depend upon the solid being periodic and can therefore be tuned by accurately controlling the nanocrystal size and surface. Interesting nanocrystal-based materials can be designed using techniques of molecular assembly (from nanocrystals/polymers composites to DNA directed assembly of nanocrystal patterns).

In particular, the study of semiconductor nanocrystals under pressure is uncovering novel mechanisms of phase transformations that shed light on important issues like crystal structure transformations, nucleation phenomena and size dependence. These processes can now be elucidated at the atomistic level by performing simulations with a recently developed constant-pressure molecular dynamics method for non-periodic systems, which combines a classical description of the pressure transmitting medium with a quantum mechanical description of the system of interest. By applying and releasing pressure, new metastable structures with non-conventional bonding arrangements can also be created.

Results will be presented for silicon and CdS nanocrystals, treated within density functional theory, tight-binding and QM/MM techniques.

Calculation of free energy surfaces in classical and ab-initio molecular dynamics

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The free energy surface of a complex system is usually characterized by the presence of deep minima separated by large barriers. Such minima correspond to distinct states of the system, and transitions among these minima reflect important changes such as phase transitions, chemical reactions and conformational modifications. Direct simulation of these processes is frustrated by the exponential dependence of the rate on the barrier height, and simulations often do not leave the free energy minimum from which they were started. In order to solve this problem we introduce a coarse-grained non-Markovian dynamics or metadynamics that can reconstruct the free energy dependence on a set of suitably defined collective coordinates. The metadynamics makes it possible to simulate in short molecular dynamics runs complex chemical processes involving several reactive steps and overcome large energy barriers in a modest amount of computer time. We illustrate the power of the method in a series of applications and demonstrate its ability to tackle a large variety of problems. In particular we show how the method can be adapted to study structural phase transitions. We also combine the metadynamics ideas with

Car-Parrinello ab-initio simulations, obtaining a very efficient method for the study of chemical reactions. Finally we show how statistical errors can be controlled and free energies of arbitrary accuracy can be calculated.

Infrared and Raman spectra of disordered oxides from first principles

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We describe a scheme for investigating infrared and Raman spectra of disordered oxides from first principles. Using first-principles molecular dynamics, we first generate an atomistic model structure of the oxide with a quench from the melt. The validity of our structural description is then examined by comparison with neutron diffraction experiments. The vibrational frequencies and modes are obtained via the dynamical matrix which is calculated by taking finite differences of the atomic forces for small atomic displacements. Through the dynamical structure factor, the vibrational properties allow us to directly compare the calculated and measured neutron densities of states. To access infrared and Raman spectra, we need to deal with the coupling to electric fields. One way of treating such couplings is achieved through the use of *finite* electric fields. For calculating the infrared spectrum, we obtain the dynamical charges from the atomic forces in the presence of a finite electric field. For the Raman spectra, we obtain the Raman tensors from the second derivative of these forces with respect to the field. We illustrate this scheme in an application to vitreous B_2O_3. We find that inelastic neutron and infrared spectra are well reproduced, while the comparison between theory and experiment is less impressive for the Raman spectrum. These results can be explained as follows. The inelastic neutron and infrared data are well described because they are related to the short-range order, which is well reproduced in our structural model. At variance, the Raman spectrum is shown to depend primarily on oxygen bending motions and is therefore more sensitive to the medium range structure. The medium range structure is evidently less well reproduced by our atomistic model. We can nevertheless extract useful structural information from the comparison between calculated and experimental Raman spectra. ¿From the intensity of the strong line at 800 cm^{-1}, we could extract an estimate for the fraction of boron atoms occurring in boroxol rings.

Electron-hole excitations in the quasiparticle and in the density-functional framework

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Ab initio calculations based on density functional theory (DFT) are a powerful tool for the study of ground state properties of even complex systems. In the case of electronic spectra, however, approaches have to be designed that extend existing methods to the description of electronic excitations. Today, two main lines of research seem to compete for the calculation of electron-hole excitations (that occur, e.g. in absorption or electron-energy loss spectroscopy): first, the GW and Bethe-Salpeter approaches, derived in the framework of many-body Green's function theory generally yield spectra in good agreement with experiment, although with a considerable computational effort. Second, time-dependent density functional theory (TDDFT) could in principle be more efficient, but suffers from the lack of reliable approximations for the exchange-correlation contributions; therefore, in particular absorption spectra of bulk materials are in general not well described.

We will compare the two approaches by investigating the meaning and importance of their various ingredients, by pointing out similarities and differences in the formalisms, and by showing results for various materials ranging from nanotubes to bulk semiconductors and insulators.

Recent progress in developments and applications of time-dependent density functional theory

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Based on the discussions of the previous talk " Electron-hole excitations in the quasiparticle and in the density-functional framework", we show that the two studied approaches are not in competition, but that their advantages should be combined in order to yield a reliable but efficient method for the calculation of electronic spectra of materials. We discuss models and an *ab inito* expression for the exchange-correlation kernel of TDDFT that have been derived from the Bethe Salpeter equation. We show that the simple models allow one to quickly estimate excitonic effects in semiconductors. Finally, the parameter-free *ab initio* kernel yields absorption spectra in semiconductors and insulators that are almost indistinguishable from the results of the Bethe Salpeter equation, for both continuum and bound excitons.

Multiple-Scale Modeling of Materials using the Quasicontinuum Method

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Atomistic and continuum methods alike are often confounded when faced with mesoscopic problems in which multiple scales operate simultaneously. In many cases, both the finite dimensions of the system as well as the microscopic atomic-scale interactions contribute equally to the overall response. This makes modeling difficult since continuum tools appropriate to the larger scales are unaware of atomic detail and atomistic models are too computationally intensive to treat the system as a whole.

We present an alternative methodology referred to as the "quasicontiuum method" which draws upon the strengths of both approaches. The key idea is that of selective representation of atomic degrees of freedom. Instead of treating all atoms making up the system, a small relevant subset of atoms is selected to represent, by appropriate weighting, the energetics of the system as a whole. Based on their kinematic environment, the energies of individual "representative atoms" are computed either in nonlocal fashion in correspondence with straightforward atomistic methodology or within a local approximation as befitting a continuum model. The representation is of varying density with more atoms sampled in highly deformed regions (such as near defect cores) and correspondingly fewer in the less deformed regions further away and is adaptively updated as the deformation evolves.

The method has been successfully applied to a number of atomic-scale mechanics problems including nanoindentation into thin aluminum films, microcracking of nickel bicrystals, interactions of dislocations with grain boundaries in nickel, junction formation of dislocations in aluminum, cross-slip and jog-drag of screw dislocations in copper, stress-induced phase transformations in silicon due to nanoindentation, polarization switching in ferroelectric lead-titanate and deformation twinning at aluminum crack tips. An overview of the methodology and selected examples from these applications will be presented.

A First-Principles Analysis of Deformation Twinning in FCC Metals

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Deformation twinning and slip are two fundamental mechanisms for plastic deformation in metals. In most metals slip dominates. Deformation twinning (DT) becomes important when the number of available slip systems is limited or at low temperatures and high strain rates. DT occurs in two phases: a critical nucleation phase followed by growth at a lower stress level. Theoretical analysis in recent years suggests that nucleation of twins most likely occurs heterogeneously at pre-existing defect sites such as grain boundaries, dislocation structures and crack tips. This talk focuses on DT nucleation at crack tips in face-centered cubic (FCC) metals. An analysis involving numerical simulation and theoretical modeling is presented.

First, atomic-scale simulations of the deformation mechanisms at crack tips in Al were carried out. The objective of the simulations was to characterize the conditions under which DT occurs at the crack tip. Al was selected because although traditionally cited as a metal that does not twin, recent experiments have shown DT at Al crack tips. It was found that for certain combinations of loading mode and orientation, DT does occur at crack tips in Al in agreement with experimental observation.

Second, a theoretical nucleation criterion for DT at crack tips based on the Peierls concept was formulated. The criterion is similar to the criterion recently introduced by Rice for dislocation emission from crack tips. The DT criterion identifies a new material parameter named the “unstable twinning energy”, in analogy to Rice’s unstable stacking energy. This new parameter controls DT at crack tips in materials. The predictions of the criterion are compared with the numerical simulations in Al and found to be in good agreement.

Finally, the theoretical criterion was used to define a new measure for the inherent “twinnability” of a material. This measure, which is based entirely on parameters that can be computed from first principles, characterizes the tendency of a material to twin relative to its tendency to deform by slip. The twinnability of 8 fcc metals was computed using parameters obtained from tight binding calculations and compared with experimental data. The agreement is encouraging.

Liquid Helium Clusters: New Experiments and Theoretical Challenges

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Despite extensive efforts by many noted theoreticians, ranging from Landau to Feynmann, the phenomenon of superfluidity in the quantum liquids 4He and 3He is still not fully understood although a large variety of computational techniques are presently available. Finite sized liquid He clusters provide simple model systems for understanding superfluidity as well as Bose-Einstein Condensation (BEC) related effects in stars and nuclei and have therefore been extensively studied theoretically. Being only extremely weakly bound small He clusters have long been inaccessible to conventional experimental probes. These problems could recently be circumvented by analyzing molecular beams of He clusters by diffracting them from nanostructured transmission gratings. Since only the wave nature is involved the method is essentially non-destructive. This technique has been further developed to make possible the measurement of the average bond distance of the He-dimer (50 Å) and its binding energy (10-3 K $\simeq$ 10-7 eV) making the dimer the largest and most weakly bound ground state molecule. The scattering of diffraction selected clusters from rare gas atoms has recently been used to determine the He-He radial distribution functions in the trimer and tetramer. These experimental results are in good agreement with recent theories.

Mixed 4He/3He clusters are also extremely weakly bound because of the smaller mass of the 3He isotope. Small clusters with three or more 3He atoms, which are being explored experimentally in our laboratory, are expected to exhibit interesting Fermi symmetry effects.

Recently the diffraction technique has been improved to facilitate measurements of the size distributions of larger clusters with N $\simeq$ 50. Surprisingly magic numbers are found which cannot be explained using the available models of nuclear and cluster physics. Recent dedicated Diffusion Monte Carlo calculations reveal that these magic numbers appear whenever the small clusters can accommodate an additional elementary excitation level. Thus very detailed experimental information on both the structure and energetics of small He clusters is now becoming available for testing theoretical models.

If time permits we will also briefly review experiments on larger He droplets with N $\simeq$ 1000 atoms. These have been successfully probed via the infra-red spectroscopy of embedded chromophore molecules. The unexpected observation of sharp rotational lines indicate that the molecules rotate freely, which is not expected for a liquid environment, and has been shown to be a new microscopic manifestation of superfluidity. An analysis of the intensities, positions, and widths of the spectral features provides deep insight into a variety of microscopic phenomena related to superfluidity.

Interfacial mixing in heteroepitaxy

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Recent results of kinetic Monte Carlo simulations will be presented, which address the question, to what extent substrate atoms will contaminate a growing film. This question is important e.g. for spintronics, where the performance of heterolayers would be spoiled by magnetic impurities in the nonmagnetic film. If the substrate atoms behave partially like a surfactant, the impurities in the growing film are most strongly correlated in the presence of Ehrlich-Schwoebel barriers, less strongly on a high symmetry surface with free interlayer diffusion and least on vicinal surfaces. The concentration profile of impurity atoms shows power-law scaling, which is also borne out by a rate equation theory. The width of the intermixed zone depends on the growth parameters, which in most cases can be explained by physical arguments.

CONTRIBUTED TALKS AND POSTERS

Molecular diffusion through proteins, M. Ceccarelli, A.Laio, M. Parrinello
ETH Zürich, Switzerland.

Ab initio calculations and thermodynamic modelling of the sigma phase in FeMo system, Jana Houserová*, Mojmír Šob*, and Jan Vřešťál**
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** Institute of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic.

Ab initio studies of structural stability and theoretical strength of transition metal disilicides with C40 structure, Dominik Legut[1,2], Martin Friák[1], Mojmír Šob[1], Jaroslav Fiala[2]
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Jahn-Teller Spectral Fingerprint in Molecular Photoemission: C_{60}, Nicola Manini, Paolo Gattari, Erio Tosatti
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A first principles study of oxygen self-defects in amorphous SiO_2, L. Martin-Samos, N. Richard, Y. Limoge, P. Paillet
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Interface states at metal/III-V(001) junctions, T. Maxisch, N. Binggeli, and A. Baldereschi
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Spin-Peierls effect and electron density in fractional quantum Hall states, Shosuke Sasaki
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TDDFT in molecules and extended systems, Ari P Seitsonen and Jürg Hutter
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Ab-initio Simulation of Self-Assembled Hybrid Nanowires, José A. Torres

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In and In-C defects in silicon, Paola Alippi
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Energetics of native point defects in 3C-SiC,
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A Preliminary Study of Carbinic Stability inside a Nanostructured Carbon Film grown by Supersonic Beam Deposition, M.Bogana (a), L.Colombo (b), and C.Bottani (a)
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Temperature Accelerated Dynamics applied to covalently bonded materials , Marco Cogoni[1], Alessandro Mattoni[1], Luciano Colombo[1], and Art Voter[2]
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Electron-transfer proteins for electronics: a theoretical study on Azurin, Stefano Corni, Francesca De Rienzo, Rosa Di Felice, and Elisa Molinari
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Surface segregation and surface order: (M)EAM predictions versus experimental results , C. Creemers, S. Helfensteyn, and J. Luyten
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Rebonding effects on noble metal surfaces : influence of stress , T.M. de Pascale and P. Ruggerone
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Structural, electronic and magnetic properties of Pd_N and Rh_N Cluster (N=2-13) , Tanja Futschek, Martijn Marsman, and Jürgen Hafner
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Ordered growth of Ag on Si(111)-(7×7) , Pavel Kocán, Pavel Sobotík, Ivan Ošťádal and Miroslav Kotrla

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CO adsorption on Rh(111): a DFT study , Lukas Köhler, Gajdos Marek, Andreas Eichler, and Georg Kresse
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Trends in the native-defect-assisted diffusion mechanisms of acceptors in silicon: B, Al, Ga, In. , Giorgia M. Lopez, Claudio Melis, Paolo Schirra, Paola Alippi,[1] and Vincenzo Fiorentini
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Quasiparticle effects in small fullerene-like GaP clusters , Giuliano Malloci[1], Giancarlo Cappellini[2], Giacomo Mulas[1], and Guido Satta[2]
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Electronic band structure of the C(111)2x1 and C(111):H surfaces. , Margherita Marsili, Olivia Pulci, Friedhelm Bechstedt, and Rodolfo Del Sole
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Vacancy- and interstitial-assisted diffusion of Ga in silicon , Claudio Melis, Giorgia M. Lopez, and Vincenzo Fiorentini
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Ab initio study of the high-pressure phase transitions cd → β-tin → Imma → sh in silicon and germanium , Katalin Gaál-Nagy, and Dieter Strauch
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Influence and intereference of induced localized states: steps and adatoms , Attilio Vittorio Vargiu and Paolo Ruggerone
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Universal tight-binding approach to semiconductors molecular dynamics simulations , Massimiliano Virdis, Luciano Colombo, and Gianni Mula

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Development of a non self-consistent tight-binding model for the computational study of hydrogenated carbon systems , Manuela Volpe, and Fabrizio Cleri
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Structure of the amorphous high-k oxide Lu2O3 , Maurizio Zaccheddu, and Vincenzo Fiorentini
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Structural and Electronic Properties of (In,Ga) (As,N) Compounds and Related Alloys , Laura Zoppi, Maria Peressi, Michele Tosolini, and Alfonso Baldereschi
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Mixed Br/CO adsorbate phases on Pt(110) , Rinaldo Zucca, and Josef Redinger
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3.1.3 Report on the 2004 "Computational Physics and Materials Science" Mini-Workshop in Gif-sur-Yvette, France

International Workshop on Computational Physics and Materials Science: "Progress in Ab Initio Computational Methods for Condensed Matter"

8–10 January 2004
CNRS Campus, Gif-sur-Yvette, France

The aim of this three-day workshop was to give a snapshot of the state of the art concerning computational methods in materials science through the presentation of some recent works. The sessions have been chosen in order to illustrate the vast applicability and the increasing complexity of ab initio calculations, and to explore their capability to deal even with systems of technological or biological interest. The workshop was also intended as a way to promote links among scientist coming from different communities and favour the exchange of ideas between distant fields, ranging from methods involving multiple time and length scales, to catalysis, or to strongly correlated materials.

The workshop was part of the series of "Total Energy"workshops started in Oxford (1983) and continued up to Trieste (2001, 2003), Miraflores de la Sierra (2000) and Tenerife (2002). The 2004 edition was organized locally by members of the theory group of the Laboratoire des Solides Irradiés (a laboratory of the CNRS, CEA and the Ecole Polytechnique) at the Ecole Polytechnique, Palaiseau, France (Valerio Olevano, Lucia Reining, Nathalie Vast). The scientific committe was composed by Alfonso Baldereschi, Stefano Baroni, Giulia Galli, Mike J. Gillan, Xavier Gonze, Jisoon Ihm, Erik Koch, Karel Kunc, Steven G. Louie, Richard Needs, Pablo Ordejon, Michele Parrinello and David Vanderbilt. The CNRS Campus in Gif (about 10 kilometers from the Ecole Polytechnique) was chosen as a very convenient site for this workshop, since Gif is well connected to Paris by public transportation, it is a pleasant place, and the Campus offers all facilities within walking distance (a guesthouse, restaurant, lecture hall, and rooms for discussions in the castle).

The workshop was attended by about 90 scientists in total, of which about 30 came from all over the world, and 60 from the Paris region. On average, every session was attended by 70 to 80 persons. In fact, as hoped the program has also attracted many researchers who are not directly working in the field, for example experimentalists who used this opportunity to get informed about ongoing developments in our community. Thanks to financial support by the ESF through

Psi-k, on top of support from CNRS, CEA, the Ecole Polytechnique, the Région Ile-de-France, and the Institut Français du Pétrole, we could cover essentially local expenses of many young researchers from European labs, and help to create an informal atmosphere through common meals and refreshments, without charging a registration fee to the participants.

In fact, the two things that have generally been most appreciated about this workshop was the quality of the talks and posters (see the program of oral contributuions below, and more details including abstracts of talks and posters at the website

http://theory.lsi.polytechnique.fr/events/workshops/gif2004.html),

and the discussions, that were particularly lively and continuous, including the official discussion time (10 minutes) after each talk, but also the coffee breaks, lunches and the poster session, involving physicists and chemists, experts and newcomers, theoreticians and experimentalists. There was also a strong participation in the round table dealing with the future of our field - that includes of course the future of our computer codes, but also, most importantly, the (uncertain) future of the young researchers!

In conclusion, one could note that the interest in ab initio calculations as a tool for the investigation of materials, complementary to experimental approaches, has increased significantly, at least in France. In a sense, it has been timely to have this workshop here in 2004. We can hope that it has stimulated at the same time an increasing exchange of ideas between experts, and increasing publicity for the potential of ab initio calculations in other communities.

Thursday, January 8th

9:00 Welcome and opening remarks.

Surfaces

9:15 **Rodolfo Del Sole** (Università di Roma "Tor Vergata", Italy): *Theory of optical and energy loss spectroscopies at surfaces.*

10:05 **Wolf Gero Schmidt** (Friedrich-Schiller-Universität Jena, Germany): *Calculation of surface optical properties: ¿From qualitative understanding to quantitative predictions.*

10:45 Coffee Break

11:15 **Hervé Toulhoat** (Institut Français du Pétrole, France): *Kinetic interpretation of catalytic activity patterns based on theoretical chemical descriptors. "Patenting the potentials, or the potential of a patent".*

11:55 Poster contributions presentation (2 minutes per contribution)

12:30 Lunch

Core Levels

14:30 **John J. Rehr** (University of Washington, Seattle, USA): *Excited State Electronic Structure and the Theory of Core-level Spectra.*

15:20 **Delphine Cabaret** (Université Pierre et Marie Curie, Paris, France): *First-principle simulations of X-ray absorption spectra for large systems Plane-wave pseudopotential approach.*

16:00 Coffee Break

Strongly Correlated Systems

16:40 **Silke Biermann** (CPHT, École Polytechnique, France): *Electronic structure calculations for materials with strong Coulomb correlations – a challenge for computational physics.*

17:20 **Stefano Fabris** (DEMOCRITOS, Trieste, Italy): *Unified LDA+U approach for pure and defective ceria.*

17:50 Poster session and reception dinner

Friday, January 9th

Nanostructures

9:00 **Steven G. Louie** (University of California at Berkeley, USA): *Theory and Computation of the Electronic, Transport and Optical Properties of Nanostructures.*

9:50 **Xavier Blase** (Université de Lyon "Claude Bernard", France): *Plastic to superconducting properties of cage-like clathrate systems.*

10:30 Coffee Break

11:00 **Maria Machon** (TU Berlin, Germany): *The strength of the radial breathing mode in single walled nanotubes.*

11:20 **Noél Jakse** (Laboratoire de Théorie de la Matière Condensée, Université de Metz, and Laboratoire de Physique et Modélisation des Milieux Condensés, France) *Prediction of the Short-Range Order of Liquid and Supercooled Metals by Ab Initio Molecular Dynamics.*

Methods involving Multiple Time and Length Scales

11:40 **Jorge Kurchan** (École Supérieure de Physique et Chimie Industrielles, Paris, France): *Supersymmetry of Langevin and Kramers equations: applications in Physical Chemistry.*

12:20 Lunch

14:00 **Stefan Gödecker** (University of Basel, Switzerland): *Structure determination of large systems: finding local and global minima of the potential energy surface.*

14:40 **Christoph Dellago** (University of Vienna, Austria): *Studying Rare Events in Complex Systems.*

15:20 Coffee Break

Magnetism and Spin Dependent Properties

15:50 **Vladimir Antropov** (Ames Laboratory, Ames, USA): *Ab-initio spin dynamics at finite temperatures.*

16:40 **Hadi Akbarzadeh** (Department of Physics, Isfahan University of Technology, Iran): *Spin Density Wave in chromium.*

17:20 Round table *(Erich Wimmer).*

Saturday, January 10th

Biological Systems

9:00 **Elisa Molinari** (Università di Modena, Italy): *Electron states and transport in biomolecules.*

9:40 **Matteo Ceccarelli** (ETH Zurich, Switzerland): *A non-markovian molecular dynamics algorithm to investigate rare events: from biological to artificial molecular machines.*

10:20 Coffee Break

10:50 **Miguel A. L. Marques** (Freie Universität Berlin, Germany): *Absorption spectra of biological systems from TDDFT*

11:30 **Francesco Gervasio** (ETHZ, Lugano, Switzerland): *Oxidative damage to DNA.*

12:00 Concluding remarks

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Abstracts

Spin Density Wave in chromium

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The peculiar magnetic properties of chromium have made it an interesting subject in condensed matter physics. The incommensurate Spin Density Wave (SDW) in ground state chromium has been extensively studied using different experimental and theoretical methods[1,2]. The experimental results indicate that simple bcc chromium, in its ground state (well below 123K), has an antiferromagnetic structure modulated by a nearly sinusoidal wave with wavelength of about 21 lattice constant and so the wave vector of SDW in (001) direction is about 0.95 of the reciprocal lattice vector.

In 1962 Overhauser applied Hartree-Fock model to an homogeneous fermi electron gas and showed that this system is unstable with respect to formation of a SDW that its wave vector connect two points in the Fermi surface of paramagnetic gas[3]. At the same year Lomer showed that the nesting property of the Fermi surface favor formation of SDW in Cr and hence one can calculate the wave vector of SDW using this Fermi surface[4].

Two approaches are commonly used to calculate properties of chromium. The direct approach is to take a large supercell containing about 21 unit cell (the wave length of SDW), and carry out the ab initio calculations within it. This time consuming approach has not yet been able to predict a correct ground state magnetic phase for chromium[5]. The second or indirect approach, which is based on the Lomer model, is to utilize the calculated Fermi surface of the paramagnetic phase to obtain the nesting vector and consequently, the magnetic properties of the system. In this method it is not needed to use supercell and hence, the calculation is much faster.

We have used the second approach to study the SDW of chromium and have investigated the effect of various parameters such as pressure and impurity on the wave vector. Our result show that Lomer model is successful in predicting a value for the SDW wave vector, which is in close agreement with the experimental result.

It has been shown experimentally that in applying pressure on the chromium, different experimental condition do not lead to a unique behavior of the system[6]. When the pressure is applied for the first time, the pressure dependence of the SDW wave vector follows the so called soft mode, having large pressure dependence, while, when the pressure is removed or reapplied up to the same pressure, the hard mode is observed, With a small pressure dependence. our calculated results are only consistent with the hard mode. It is not yet clear to us whether this deficiency roots in Lomer model, or it has some other sources.

Secondly, we doped V, Fe, Co, W and Mo impurities in chromium and calculated the rate of change of SDW wave vector with respect to the concentration. For this investigation we used a simple model, which is based on an assumption that the impurities do not affect the band structure of pure chromium and they only modify the Fermi energy location. Our results are in qualitative agreement with available experimental data and have the correct signs[1].

Finally, we calculated the magnetic hyperfine interaction at impurity sites in Cr15X alloys (X=Rh, Cd, Sn).

All of our calculations were performed by WIEN2k code that is a full-potential LAPW package based on DFT[7].

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Ab-initio spin dynamics at finite temperatures

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A theoretical analysis of magnetic order as function of temperature magnets is performed using time dependent density functional theory of spin dynamics. We will show that such 'hydrodynamic' spin dynamics allows to describe low temperature quantum effects and high temperature classical behavior in framework of one consistent approach. We demonstrated that the effects of quantum statistics can be included in simulational scheme. Our first applications for 3d magnets revealed a giant short range order specific for itinerant magnets. The existence of a such order allows us for the first time to resolve several longstanding problems in magnetism theory: the high temperature susceptibility and the critical temperature of magnetic phase transition in itinerant magnets. A critical analysis of time dependent density functional theory and a corresponding comparison with other techniques will be demonstrated. I will discuss a significance and coexistence of intraatomic coulomb correlations and short range order effects in magnetic systems.

Ab initio Calculated Electronic, Magnetic, and Structural Properties of Fe/GaAs(001) Junctions

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The electronic and magnetic properties of Fe/GaAs(001) have been computed by means of the first-principles full potential linearized augmented plane-wave method (FLAPW). The effects of the atomic relaxation and the diffusion at the interface on the electronic and magnetic properties will be discussed. In particular, it is shown that the atomic relaxations increase the Fe magnetic moment at the interface for the case of F/Ga interface and reduce it for that of Fe/As interface. This effect was explain by band hybridization effects by computing and analyzing directional density of states of neighboring interface atoms. In addition, the atomic relaxations are shown to have a tendency to exchange the Fe by Ga or Fe by As at the interface. This behavior led us to exchange As with Fe. The result of this exchange resulted on the discovery of the so-called dead magnetic layer of Fe at the interface. We have computed the X-ray magnetic circular dichroism (XMCD) at the Fe $L_{2,3}$ edge and found that the results are strongly related to the different situation obtained by direct calculations of the ground state properties. The XMCD spectra can be compared directly with experimental results.

Electronic structure calculations for materials with strong Coulomb correlations – a challenge for computational physics

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Density functional theory in the local density approximation (LDA) has led to tremendous progress in our ability to describe or even *predict* materials properties within a general theoretical framework. It fails, however, rather spectacularly in "strongly correlated materials" where effects associated with the Mott phenomenon, that is electronic localization due to interactions, are essential. A combined electronic structure – many body method, "LDA+DMFT", that supplements band structure theory with a dynamical mean field (DMFT) treatment of many body effects has proven successful in these cases.

We will give an overview of these developments, including some recent examples [1], but also give a critical account of the shortcomings of the LDA+DMFT method. Finally we will discuss recent developments towards a first principles approach to strongly correlated materials based on ideas from the GW approximation and dynamical mean field theory [2] This "GW+DMFT" approach combines a GW-inspired description of screening with the ability of DMFT to deal with interactions of arbitrary strength.

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Plastic to superconducting properties of cage-like clathrate systems.

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We will first review of few properties of silicon clathrates. Si clathrates are cage-like materials composed of face-sharing Si_20, Si_24 and/or Si_28 cages. All atoms are in a four-neighbors sp^3 hybridization, as in the diamond phase, but unlike this latter structure, a significant doping (or intercalation) is allowed by placing selected atoms (Ba, I, Na, etc.) inside the cages. We will show that silicon clathrates (a) can exhibit a direct band gap in the visible range (from 1.9 to 2.4 eV GW value) [1] and (b) that the sp^3 network can lead to $T_c = 8$ K BCS-type superconductivity in a strong coupling regime of $\lambda \sim 1$ [2]. Further, the properties of the hypothetical carbon clathrates will be predicted. The electron-phonon coupling potential will be shown to be much larger than in fullerenes [2]. Finally the mechanical ideal strength of carbon clathrates will be compared to that of diamond.

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Effective Hamiltonians in condensed matter: a first principles many-body approach

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The effective Hamiltonian methods in condensed matter, such as the crystal field or the cluster approaches, divide the sytem into a strongly interacting part and an environment, and use parameters to model the interaction with the environment. An effective Hamiltonian is built, which gives a detailed representation of the strongly interacting part, and treat the environment as a perturbation. The main drawback of this approach is the fact that the parameters cannot be calculated ab initio.

Using many-body theory, we build a first principles self-consistent effective Hamiltonian, where all parameters are caculated.

Standard many-body theory considers the initial state as a single non degenerate Slater determinant. To set up an effective Hamiltonian, it is necessary to take into account a space V of initial states. The dimension of V is the dimension of the Hamiltonian. Then a hierarchy of Green functions is derived. This hierarchy is closed to get the desired self-consistent equations. The hierarchy reproduces the standard many-body results for a space V of dimension 1, and its first order approximation reproduces the standard crystal field equations.

This formalism is expected to be efficient for systems that are well represented by the crystal field formalism, such as the optical properties of transition metal impurities or the magnetic properties of rare earths.

Excited states of Cu_2O within GW approximation

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Cuprous oxide has been extensively studied during the last decades, mainly because of its exciton series in the optical range. Cu_2O is a good starting point to address the fundamental issue of transition metal oxides. Indeed, this material has a cubic structure, a closed d shell, and is non-magnetic. The topic of transition metal oxides is now very important: it is known that density functional theory fails to predict a gap in various insulating oxides like CoO, CuO, Ti_2O_3.

We performed DFT and GW calculations using a plane-wave basis set and the pseudopotential technique. We carefully studied the role of semicore states ($3s^2 3p^6$). Though deep in energy, these states have a large overlap with valence bands. Their influence is drastic on structural properties, but slight on the Kohn-Sham band structure. We show that the semicore states have to be included in the GW calculation to get meaningful results.

Even a "correct" GW calculation underestimates largely the intrinsic gap. We discuss the causes of this failure.

Excitons in carbon nanotubes: a first-principles study

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The nature of optical excitations in carbon nanotubes and their dimensionality remain an open question. On the experimental side, it is now possible to carry out optical spectroscopy on nanotubes of selected sizes and types.[1] The results indicate that single-particle schemes are not sufficient for their interpretation. On the theoretical side, interesting phenomenological approaches were applied[2], but a realistic and quantitative calculation of the actual excitonic binding energy and spatial size requires an *ab initio* approach.

In this work, we present the results of our calculations of excitonic effects an d optical properties of carbon nanotubes. We adopt a first-principles approach and use many-body methods such as the Bethe-Salpeter Equation (BSE), which has been used with considerable success to calculate excitonic effects in bulk semiconductors[3,4,5] and most recently, in one-dimensional systems, such as polymers.[6] The success of the latter reinforces the applicability of the BSE to one-dimensi onal systems such as nanotubes. The novelty of our approach consists in the symmetry analysis of the nanotube in which we take advantage of the invariance of the tube with respect to screw-symmetry operations. Such an analysis not only reduces the computation effort required, but also offers a better understanding of the physics involved, including the nature of the excitons and of the optical transitions. We show results for the optical spectra, exciton binding energy and wavefunctions for selected nanotubes, and use them to discuss trends in exciton dimensionality as a function of nanotube size and geometry.

First-principle simulations of X-ray absorption spectra for large systems. Plane-wave pseudopotential approach.

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X-ray absorption spectroscopy (XAS) is a powerful technique for structural end electronic studies of materials. The extended region of a XAS spectrum, called EXAFS, gives quantitative information about the local range order around the absorbing atom (coordination number, interatomic distances). The near-edge region, called XANES, provides qualitative information

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about the atomic arrangement up to the medium range (i.e. ≈ 8 Å around the absorbing atom). XANES spectroscopy is sensitive to the electronic structure (nature of chemical bounds, orbital hybridizations, valence state of the absorbing atom, etc). It is indeed considered as a tool to probe empty states in solids.

The interpretation of XANES is not straightforward, as compared to that of EXAFS. Indeed XANES analysis often requires sophisticated simulation tools. In the case of K-edges, real-space multiple scattering theory has been extensively used in the past twenty years. However, multiple scattering theory has traditionally suffered from a drawback, i.e., the "muffin-tin" approximation of the potential. I will present a "non muffin-tin" scheme for calculating XANES spectra. The method uses periodic boundary conditions, plane-wave basis-set, pseudopotentials and reconstructs all-electron wave functions within the Projector Augmented Wave (PAW) framework. The use of a Lanczos basis and of the continued fraction permits the calculation of XANES spectra in large supercells (hundreds of atoms). The cross section is implemented in both electric dipole (E1) and electric quadrupole (E2) approximations.

Several applications on oxide minerals will be shown. In particular, I will present calculations at the K-edge of paramagnetic impurities (Cr, Fe, Ti) in α-Al_2O_3 (i.e. ruby and sapphires). The influence of core-hole effects and of spin polarization will be investigated. Furthermore, some examples of pre-edge calculations (containing both E1 and E2 transitions) will be presented. Finally, comparison will be made with recently developed Bethe-Salpeter approach.

A non-markovian molecular dynamics algorithm to investigate rare events: from biological to artificial molecular machines

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We present the application of a novel method to investigate rare events. As an example we considered the translocation of an antibiotic molecule through a protein channel and the conformational change of a molecular switch in solution upon oxido-reduction. An empirical force field was used in both examples.

The method consists of an history-dependent molecular dynamics where one or more order parameters are choosed to guide the process at a coarse-grained level, but with an all-atom description to evaluate forces on them. With a defined frequency a repulsive potential is added to the Hamiltonian preventing the system to re-visit conformations described by the instantaneous values of the order parameters. This allows to escape from free energy minima. Moreover the accumulated repulsive potentials, with the sign inverted, give the free energy dependence on the order parameters.

The algorithm is general enough to be extended to other systems even with an ab-initio descritpion of interactions, such as chemical reactions in solution or on surfaces, defect transformations in solids.

On the incorporation mechanism of water in α-quartz

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It is well known that the presence of water in α-quartz has extremely influence on a wide range of geological processes. Water in α-quartz can affect its mechanical properties and lead to hydrolytic weakening and cracking. Water in α-quartz has been subject of several studies in the past years, but its incorporation mechanism is not completely understood yet. In this work we have investigated incorporation of water in α-quartz using density-functional theory (DFT). Generalized gradient approximation (GGA) was used to determine the atomic geometry and thermodynamic properties of water related defects in α-quartz. We found that water is incorporated by forming hydroxyl groups at low temperature. We also found that the choice of the water chemical potential plays an important role in predicting the stability of structures.

Ab Initio Characterization of the Cubic, Tetragonal, Monoclinic and Rutile Phases of Zirconia by Different Spectroscopic Techniques

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In this work, we aim to predict, with the aid of ab initio calculations, spectra obtained by different experimental methods (Bremsstrahlung isochromat spectroscopy (BIS); X-ray absorption spectroscopy (XAS); electron energy loss spectroscopy (EELS); Raman spectroscopy) and to determine which is the most appropriate spectroscopic method to characterize the different phases of zirconia (ZrO2).

We have studied the fundamental state of pure zirconia. The relative stabilities of the cubic, tetragonal and monoclinic phases have been obtained using Density Functional Theory (DFT) in the local density approximation (LDA). The theoretical results are in good agreement with experimental data, contrary to results obtained for the rutile and anatase phases of TiO2, where the theoretical stability does not agree well with experiment. We discuss the results obtained for the equations of state of the different phases.

The electron energy loss spectra (EELS) have been calculated using Time-Dependent Density Functional Theory (TDDFT), and are compared to experimental results. In particular, we discuss the effect on the spectra which could be obtained by different methods (BIS, XAS, EELS and Raman) of the evolution of the coordination of the zirconium atom from Z=6 in the cubic and tetragonal phases to Z=7 in the monoclinic phase and to Z=6 in the hypothetical rutile phase.

Assessment of competing mechanisms of the abstraction of hydrogen from CH_4 on Li/MgO(001)

L. K. Dash and M. J. Gillan

First-principles calculations based on the DFT-pseudopotential method with plane wave basis sets are used to study the energetics of H abstraction from CH_4 on the Li-doped MgO(001) surface. Experimental work has led to the proposal of two competing mechanisms for the reaction: either direct interaction of CH_4 with an O^- hole state bound to the Li dopant, or interaction of CH_4 with a surface F centre whose charge state is modified by the presence of the dopant. The calculations are performed in periodically repeated slab geometry, with attention given to system-size errors. For direct interaction with the hole state, the calculations indicate that the reaction is weakly endothermic, by about 0.2eV, but for the F-centre mechanism it is endothermic by over 1eV. Even allowing for likely DFT errors of a few tenths of an electron volt, this gives strong evidence against the F-centre mechanism.

Studying Rare Events in Complex Systems

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Computational studies of processes occurring in complex systems are often complicated by a wide separation of time scales. Examples include the nucleation of first-order phase transitions, chemical reactions in solution, diffusion on surfaces, and protein folding. To bridge this time scale gap various approaches have been put forward. I will discuss some of these techniques focusing on computational methods to treat rare transitions between known stable states.

Theory of optical and energy loss spectroscopies at surfaces

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The theory of surface optical spectroscopy is briefly reviewed. The reduced symmetry of most surfaces allows one to extract the anisotropic surface contribution from the much greater, but isotropic in cubic crystals, background reflectance due to the bulk. Hence Reflectance Anisotropy Spectroscopy (RAS) is a widely employed technique for surface optical spectroscopy. DFT Kohn-Sham states are used to calculate the matrix elements of the momentum operator between filled and empty states, which yield the transition probabilities. Self energy effects can be

embodied according to the GW approximation. The electron-hole interaction, which is essential to obtain accurate theoretical spectra, can be accounted for by solving the Bethe Salpeter equation. However, its computational complexity makes it doable only for the simplest surfaces. Some examples are given, which show good agreement with experiments.

Electron energy loss spectroscopy is much more sensitive to surfaces; however, its theoretical description requires the inversion of the nonlocal dielectric function, which is a formidable task in itself. Hence, calculations are usually carried out within the local three-layer model. The electron-hole interaction has never been included so far in energy loss calculations for surfaces.

Unified LDA+U approach for pure and defective ceria

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We present ab-initio density functional calculations which for the first time allow to treat pure and defective structures of cerium oxide in a unique theoretical framework. The problem of describing electron localization at Ce crystal sites, which occurs when stoichiometry departs from the CeO $_{2}$2 phase, without *a priori* assumptions on the defectchemistry itself, is solved by adding a Hubbard U term to the traditional density functional. The parameter U is calculated variationally. The method correctly predicts the atomistic and electronic structures of the CeO_2 and Ce_2O_3 bulk phases, as well as the subtle defect chemistry in reduced materials CeO_{2-x}, which controls the oxygen storage functionality of cerium-based oxides.

Elementary processes during the epitaxial growth of oxides: the case of MgO

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Metal oxides are nowadays used in many applications (microelectronics, gas detection, magnetic devices, etc). They may appear as epitaxially grown thin films on various substrates, as substrates, or both of them. As a consequence of the intense and rapidly varying microscopic electrical field, their electronic properties are very sensitive to the atomic structure, such as the surface flatness and to the details of the interfaces with other materials. The understanding of the basic mechanisms that play a role during the growth (adsorption, diffusion, evaporation, etc.) is therefore crucial.

In this paper we focus on oxide on oxide growth studied by means of first-principles and empirical simulations. To this purpose, we performed an overall study of the corresponding elementary processes in the prototypical case of MgO homoepitaxy on the MgO(001) surface [1], considering as deposited species atoms (Mg,O) or small molecules (O_2, MgO, MgO_2) that may occur in molecular beam epitaxy or sputtering.

We show that the energy landscape that is seen by the diffusing species is determined by the local electronic and atomic structures, to a large extent. For instance, diffusion close to atomic steps is qualitatively and quantitatively different from that on flat terraces. Moreover, the study of various charge-transfer reactions between the ad-molecules and/or the ad-atoms reveals that the actual surface stoichiometry results from a subtle interplay between the reactivity of the involved species and their diffusing behaviour. The computed core-level shifts of the ad-species can be compared to the outcome of X-ray photoemission spectra taken during the growth, which enables the identification of the ad-species on real samples.

The atomic and electronic structures of flat ad-clusters Mg_nO_m ($2 < n, m < 5$) are also studied. Finally, we outline a possible scenario for large-scale homo-epitaxy and compare our simulations to the available experimental data. A special emphasis is put on the perspectives of linking our atomic-scale calculations with the macroscopic models that are usually employed to describe the crystal growth. In particular, we show that those models must be generalized to account for the larger complexity of the chemistry and the physics at oxide surfaces, compared to elemental crystals.

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Multi-scale modeling of the defect population evolution in electron irradiated alpha-iron

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We have performed a multi-scale modeling of the evolution under isochronal annealing of the defects produced by electron irradiation in alpha-Fe. The stability and mobility of the relevant point defects and defect clusters (vacancies, self-interstitials and small clusters of vacancies or intertitials) are first determined by the SIESTA ab initio method using supercells with 128 atoms. These calculations were made possible by developing a suitable basis set for Fe and by improving the performance of the SIESTA code for metals. The speed-up factor with respect to plane-wave codes allowed us to study a large number of defect configurations as well as migration paths. These results are then used as input data for an event-based kinetic Monte Carlo model to simulate the defect-population evolution after low temperature electron irradiation: defects may migrate, aggregate, dissociate or annihilate. We followed closely the conditions of existing experiments, where changes in the defect population are evidenced by abrupt variations in the resistivity of the sample (so-called recovery stages). We successfully reproduce all the recovery stages and we clearly attribute them to the migration or dissociation of specific defects. Dose effects, i.e. shifts of the recovery stages when the irradiation dose is increased, are also properly reproduced.

Oxidative damage to DNA

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Oxidative damage of DNA via radical cation formation is a common cause of mutagenesis, and elaborate defense systems against its effects exist in almost all organisms. Based on state-of-the-art ab-initio molecular dynamics simulations, we suggest the existence of a steering mechanism that guides the first steps of this oxidation process toward a unique product. In the mechanism proposed here, guanine, which among the bases has the lowest oxidation potential, and the phosphate backbone play a crucial role. We found that guanine, losing one of its protons to cytosine, acts as a radical state sink, causing the localization and stabilization of an otherwise delocalized state. After this first step a chain of reactions, leads to a specific radical precursor to the most common oxidation product found in DNA: 8-oxo-guanine. The rate limiting step is the water protolysis. We illuminate the role of the local environment in considerably lowering the barrier. Of particular relevance in this respect is the role of the phosphate backbone.

Prediction of the Short-Range Order of Liquid and Supercooled Metals by Ab Initio Molecular Dynamics

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The understanding of the short-range order (SRO) of liquid and supercooled metals is a fundamental problem in relation to nucleation phenomena[1]. ¿From the early studies of Frank[2], it is believed that the icosahedral packing can explain deep undercooling effects in metallic liquids. Recent neutron scattering experiments[3] on Ni, Fe and Zr have revealed a quite pronounced icosahedral SRO already in the stable liquid, which reinforces in the supercooled region, although it has been argued that larger polytetrahedral structures yield to a better description of the structure factors for these metastable states.

In this work, we report results of a series of ab initio molecular dynamics simulations (MD) for liquid Ni, Zr and Ta to investigate the local structure and its evolution upon supercooling. Such first-principles based simulations provides an accurate and powerful theoretical tool to study consistently structural, dynamic and electronic properties of these metals containing d-electrons. Using the common-neighbour analysis[4], giving a three-dimensional picture of the inherent structures from the simulations, we have found an evolution upon supercooling which depends on the system under consideration. For Ni[5], undercooling is accompanied by the occurrence of a complex polytetrahedral SRO that consists of more numerous Frank and Kasper polyhedra[6] (Z14, Z15 and Z16) larger than the simple icosahedron. This is also true for Zr, but in this case, we show that a strong competition exist with the bcc-like SRO which increases with the degree of supercooling[7]. For Ta, the results give a strong support to the occurrence of a metastable A15 phase upon supercooling[8].

Finally, it is worth mentioning the case of covalent metals such as Si for which undercooling gives rise to a completely different behaviour. We have shown[9] that the tetrahedral ordering reinforces and the coordination number decreases, which has implications for the liquid-liquid phase transition towards a low-coordinated liquid, as shown recently by empirical MD simulation[10].

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Atomistic mechanism of proton conduction in solid $CsHSO_4$ by first-principles study

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The electronic structure and proton transfer mechanism of the solid $CsHSO_4$ in the phase I with a tetragonal structure and the phase II with a monoclinic structure have been studied by the first-principles method based on the density functional theory (DFT). The calculated results show both phases have similar properties in the electronic structures including the density of states and the band gap. Proton transfer paths and barriers have been investigated by the transition state theory. The similarities and differences of proton transfers in both phases have been discussed. For the phase I, the calculated results indicate that the reorientations of the sulfate tetrahedrons can take place very frequently, which is in accordance with the experimental observation. For the phase II, the highly ordered hydrogen-bond network makes the reorientation of the tetrahedron very difficult. The relatively disordered hydrogen-bond network in the phase I makes the reorientation quite easy, which speeds up proton transfer significantly. The atomistic proton-transfer mechanism in the phase I is proposed.

Quasiparticles from quantum Monte Carlo: Effective mass and Wilson ratio for K_3C_{60}

Erik Koch and Olle Gunnarsson
Max-Planck-Institut für Festkörperforschung,
Stuttgart

Taking advantage of the fixed-node approximation to stabilize excited states, we calculate quasiparticle energies by quantum Monte Carlo. We apply this approach to a model describing K_3C_{60} and show that it works surprisingly well. We determine how the quasiparticle dispersion changes with increasing correlation and compare to the many-body enhancement of the Pauli susceptibility. While the self-energies for our model seem to depend only weakly on the momentum (and band-index), we find a Wilson ration that appears to behave qualitatively different from what is expected from dynamical mean-field theory.

Supersymmetry of Langevin and Kramers equations: applications in Physical Chemistry

Jorge Kurchan
École Supérieure de Physique et Chimie Industrielles, Paris, France

Langevin and Kramers processes can be immersed in a larger frame by adding fictitious fermion variables. The (super)symmetry of this larger structure has been used to derive Morse theory in an elegant way. The original physical diffusive motion is retained in the zero-fermion subspace. Subspaces with non-zero fermion number which yield deep information, as well as new computational strategies for barriers, reaction paths, and unstable states – even for non-zero temperatures. I will attempt a self-contained presentation.

First principles calculation of vibrational Raman spectra in large systems

Michele Lazzeri and Francesco Mauri
Laboratoire de Mineralogie Cristallographie de Paris,
and Universite Pierre et Marie Curie

We present an approach for the efficient calculation of vibrational Raman intensities in periodic systems within density functional theory[1]. The Raman intensities are computed from the second order derivative of the electronic density matrix ρ with respect to a uniform electric field. In contrast to previous approaches, the computational effort required by this method for the evaluation of the intensities is negligible compared to that required for the calculation of vibrational frequencies. The second-order derivatives of ρ are obtained through an original formalism we recently developed[2], which allows the straightforward treatment of uniform-electric-field perturbations in extended insulators. As a first application, we study the signature of 3- and 4-membered rings in the the Raman spectra of several polymorphs of SiO2, including a zeolite having 102 atoms per unit cell.

[1] M. Lazzeri and F. Mauri, Phys. Rev. Lett. vol. **90**, 036401 (2003).

[2] M. Lazzeri and F. Mauri, Phys. Rev. B vol. **68**, 161101(R) (2003).

Theory and Computation of the Electronic, Transport and Optical Properties of Nanostructures

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The restricted geometry and symmetry of nanostructures often give rise to interesting quantum confinement, enhanced many-electron interaction, and other effects related to reduced dimensionality. These effects can lead to novel physical properties and phenomena, which also are potentially useful in applications. In this talk, I discuss how theory and computation have provided understanding to some of the unusual electronic, transport, and optical properties of nanotubes and molecular junctions. Several selected examples are presented. The quantum conductance of metallic carbon nanotubes is very robust against defects, and nanotube junctions form interesting nanoscale device elements. The band gap of BN nanotubes may be tuned with transverse electric fields via a giant Stark effect. The optical spectra of small diameter carbon nanotubes exhibit dramatic excitonic effects. Molecular dynamics studies show unexpected behaviors in the dissipation of mechanical energies in nanostructures (friction on the nanoscale). Finally, molecular electronic devices, i.e., electrical transport through a single molecule, can produce highly nonlinear I-V characteristics. The physical mechanisms behind these unusual behaviors are examined.

The strength of the radial breathing mode in single walled nanotubes

M. Machon, S. Reich, J. Maultzsch, P. Ordejon, and C. Thomsen
TU Berlin, Germany

Since their discovery, carbon nanotubes have attracted the attention of scientists due to their unusual physical properties and their potential applications. A major challenge is the characterization of the nanotube diameters and chiralities present in a sample. Raman measurements of the diameter-dependent radial-breathing-mode (RBM) frequency seem to be a candidate technique to solve this problem. We present ab initio calculations of the RBM electron-phonon coupling matrix elements for several nanotubes. Using the SIESTA package, we calculated the phonon spectrum and equilibrium electronic band structure. We studied the band energy shift caused by the deformation of the nanotube due to the radial breathing mode, which yield the electron-phonon coupling matrix elements. We obtain a systematic dependence of the matrix elements on diameter and chirality, which suggests the use of the Raman intensity as additional information for sample characterization.

Absorption spectra of biological systems from TDDFT

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Freie Universitt Berlin, Germany

Not surprisingly, the theoretical understanding of biophysical processes is a very active field of research. In particular, there have been spectacular advances in the characterisation of structural and dynamical properties of complex biomolecules by a combination of quantum-mechanical and classical-molecular mechanics methods (QM-MM). However, and in spite of the large amount of experimental work in photo-active molecules, the theoretical description of the interaction of these molecules with external time-dependent fields is very much in its infancy. Photo-active molecules relevant for biology include the green fluorescent protein (GFP), retinal, chlorophyll, etc. On the other hand, time dependent density functional (TDDFT) theory has proved to be an invaluable tool for the calculation of excitation spectra of molecules. We will present a way to combined QM-MM methods (for the ground state) with TDDFT (for the description of the excited states) to calculate optical absorption spectra. Our first test case, the GFP, yielded remarkably good results. Very recent work on azobenzene and on the DNA basis will also be reviewed.

Valence Band Offset in Mo/SiO$_2$ structures

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The continued scaling of CMOS devices presently calls for a fundamental change in transistor gate stack materials. In addition to SiO$_2$ replacement by high-k dielectrics, the use of poly-silicon as the gate electrode has been questioned. Between the possible candidates to gate electrode, the Molybdenum displays some interesting features, like the wide range values of its work function that can be attained by mean of ion implantation.

In this work, we report progresses on *ab-initio* calculations of the valence band offset (VBO) of Mo/SiO$_2$ structures. The VBO is split in two terms:

$$\Delta E_{VBO} = \Delta E_v + \Delta V, \tag{1}$$

where ΔE_v is the band-structure term, that is, the difference between the two band edges of the constituent materials, and ΔV is the lineup of the electrostatic potential generated by the electronic pseudo-charge and by the charge of the bare ion cores. The ΔV term is obtained by making a macroscopic average of the Kohn-Sham Potential, that in turn is periodic. The calculations were carried out in the framework of the density functional theory (DFT). First, we perform simulations on a relatively small system consisting of 5 layers of bcc Molybdenum plus 4 cristobalite SiO_2 layers, allowing atomic relaxation. Second, we analyse the effect of increasing the number of SiO_2 and Mo layers on the VBO, without relaxation of the atomic coordinates. In the SiO_2 layers, a residual non-negligible electric field develops, because of non-equivalence of the two Mo/SiO_2 interfaces present in the supercell. Finally, we discuss the impact of this effect on our results.

Ab-initio study of the neutral self-defects in a silica glass

L. Martin-Samos[1], Y. Limoge[1], J.P. Crocombette[1], G. Roma[1], N. Richard[2]
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[2]*CEA-DIF, Bruyère-Le-Châtel*

In the context of a general study on aging of nuclear glasses, we present a characterisation of the neutral self-defects in a silica model and the first results on the self-diffusion mechanism. Due to the intrinsic disorder in the glass and then, the requirement to calculate a statistic, it is necessary to use a fast and accurate ab-initio method. We choose an ab-initio code based on Localised pseudo-Atomic Orbitals basis set SIESTA [1,2,3]. To test the validity of the basis set choose we compare the SIESTA results with VASP [5,6,7] and PWSCF [4]. We will show the self-defects formation energy distributions (self-interstitials and vacancies of oxygen and silicon) and the structures. We will also discuss the origin of these energy distributions and the nature of the principal diffusion mechanism as a function of the oxygen partial pressure.

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[2] P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. **53**, BR10441 (1996).

[3] E. Anglada, J. M. Soler, J. Junquera and E. Artacho, Phys. Rev. **66**, B205101 (2001).

[4] S. Baroni, A. Dal Corso, S. de Gironcoli and P. Giannozi, http://www.pwscf.org

[5] G. Kresse and J. Hafner, Phys. Rev. B **47**, RC558 (1993).

[6] G. Kresse and J. Frthmuller, Phys. Rev. **54**, B11169 (1996).

[7] G. Kresse and J. Joubert, Phys. Rev. **59**, B1758 (1999).

Excited State Electronic Structure and the Theory of Core-level Spectra

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There has been dramatic progress in recent years both in ab initio calculations and the in interpretation of various core level x-ray and electron spectroscopies [1]. We begin by discussing the theory based on the close connection between core-level spectra and excited state electronic structure: both are related to a Green's function for an excited photoelectron in the presence of a core-hole, leading to a "standard" quasi-particle model for excited state calculations. We focus on the real-space Green's function approach which is the real space analog of the KKR band structure method. This approach has been implemented in efficient ab initio codes, such as FEFF8, which incorporate the most important many-body effects and and permit an interpretation in terms of geometrical and electronic properties of a material. We also discuss extensions to the theory which go beyond the independent-particle approximation. These include time-dependent density functional theory (TDDFT) which treats local field effects, and an effective Green's function theory which includes excitations beyond the quasi-particle approximation. Finally we discuss recent improvements based on fast, parallel algorithms which have made large scale ab initio core-level calculations practical in aperiodic systems with of order 1000 atoms [2]. These developments are illustrated with a number of applications to x-ray absorption spectra (XAS) and electron energy loss spectra (EELS) from the far UV to x-ray energies.

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[2] A. L. Ankudinov et al., Phys. Rev. B **65**, 104107 (2002).

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Ab-initio DFT Studies on the Interactions of Selected Biologically Active Molecules with Heme Prostetic Group

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Both the chemistry and biology of the heme complexes are of a great biological importance. This is due to the fact that they are formed in vivo and are believed to be responsible for numerous physiological and pathophysiological effects. Consequently, they are subject to many experimental studies. Theoretical investigations of their geometric and electronic structure are not so frequent and usually limited to quite small models. Here, the full-size six and five coordinate heme complexes with selected small molecules, namely NO, CO, O2, NO2-, and H2O, are studied by means of quantum chemical DFT method within both LDA-VWN and GGA-RPBE functionals. Kohn-Sham orbitals are described by extended all-electron basis sets of contracted Gaussians. For each complex the optimal geometric structure is obtained. The electronic structures of complexes are described in terms of Mulliken charges and Mayer bond indices. Obtained results allow one to conclude that the bond between iron and a small molecule is the strongest in the case of carbonyl complex and the weakest in Fe(heme)(his)NO2 system. In addition, the latter has a positive binding energy, which means that the bond is unstable and should spontaneously undergo dissociation. This result supports the proposed mechanism for reductive nitrosylation of ferrihemoproteins. It is claimed that once the heme-NO2 adduct is formed, the Fe-NO2 bond is broken and five-coordinate heme complex binds NO present in solution. Moreover, the analysis of the parameters defining the iron-histidine bond indicates that this bond is longer and weaker in nitrosyl and carbonyl complexes than in the systems with the O2, NO2-, and H2O molecules as ligands. The shortest and, what follows, the strongest bond occurs in aqua complex. The energy needed to split this bond is negative in case of Fe(heme)(his)NO compound, which means that this bond is thermodynamically unstable and the histidine dissociation process is favored. This confirms the hypothesis of the mechanism of sGC activation by the elongation of the bond, followed by its dissociation. Although the energy of the iron-histidine bond in Fe(heme)(his)CO is higher, other parameters of the bond (length and bond order) suggest that the first step of the enzyme activation by CO may be the same and may consist of the weakening of the bond similarly as during the activation by NO. Finally, the analysis of charge changes induced by the binding of the small molecules to the Fe(heme)(his) complex point out the role of the heme ring as a reservoir of electrons in the studied complexes.

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Tight-binding study of the strain effects on the electronic properties of InAs/GaAs quantum dots

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

We present an atomistic investigation of the strain effects on the electronic properties of quantum dots (QD's) within the empirical sp^3s^* tight-binding (TB) model with interactions up to 2nd nearest neighbors and spin-orbit coupling. Results for the model system of capped pyramid shaped InAs QD's in GaAs, with supercells containing $\sim 10^5$ atoms are presented and compared with previous empirical pseudopotential results; the good agreement found shows that TB is a competitive tool for a realistic treatment. The strain is incorporated through two different approaches : the continuum elasticity theory and the atomistic valence force field model, which are combined. The TB treatment allows for the effects of bond length and bond angle deviations from ideal InAs and GaAs zincblende structure to be selectively removed from the electronic calculation, giving quantitative information on the impact of strain effects on the bound state energies and on the electron and hole wave function confinement inside the dot. Effects of dot-dot coupling have also been examined to determine the relative weight of both strain field and wave function overlap.

Calculation of surface optical properties: From qualitative understanding to quantitative predictions

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Optical spectroscopies are emerging as powerful and exquisitely sensitive to probe surfaces, with many potential applications in determining surface structure or monitoring the growth of materials. However, the interpretation of surface optical spectra is not at all straight forward and may even be counter-intuitive. It requires either comparisons of with already understood spectra for similar structures or detailed calculations of the line shape. Unfortunately, calculations of surface optical properties are numerically very demanding and, therefore, have not always been very helpful in understanding and predicting the surface optical response. Thanks to the computational and methodological progress in the last couple of years, however, it has now become possible to calculate surface optical spectra accurately and with true predictive power. This allows on one hand for a much better understanding of the origin of specific features such as certain surface optical anisotropies. On the other hand, a good agreement between the measured and the calculated spectra offers conclusive confirmation of the surface structure. In this talk I will focus on the simulation of Reflectance Anisotropy Spectroscopy (RAS) for semiconductor surface structures and will discuss recent methodological advances, which allow for the modeling of self-energy, excitonic and local-field effects in large and complex systems. It is demonstrated to what extent transitions between surface states, surface defects, surface-induced strain and surface electric fields cause measurable optical anisotropies.

*in collaboration with PH Hahn, K Seino, F Bechstedt, S Wang, W Lu, and J Bernholc

Parameter-free calculation of response functions in time-dependent density-functional theory

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We have established and implemented a fully *ab initio* method which allows one to calculate optical absorption spectra of semiconductors and insulators, including excitonic effects, without solving the cumbersome Bethe-Salpeter equation, but obtaining results of the same precision. This breakthrough has been achieved in the framework of time-dependent density-functional theory, using new exchange-correlation kernels f_{xc} that are free of any empirical parameter. We show that the same excitonic effects in the optical spectra can be reproduced through different f_{xc}'s, ranging from frequency-dependent ones to a static one, by varying the kernel's spatial degrees of freedom. This indicates that the key quantity is not f_{xc}, but f_{xc} combined with a response function. We present results for the optical absorption of bulk Si, SiC (exhibiting continuum exciton effects) and bulk Argon (exhibiting instead a bound exciton series) in good agreement with experiment, almost indistinguishable from those of the Bethe-Salpeter approach.

Kinetic interpretation of catalytic activity patterns based on theoretical chemical descriptors.
“Patenting the potentials, or the potential of a patent”

Hervé Toulhoat
Institut Français du Pétrole, France

We have shown previously that “volcano curves” can be obtained when activity patterns, conveying experimental information on periodic trends in catalysis by transition metal sulfides, are correlated with bond energy descriptors calculated for ideal bulk solids at the DFT/GGA level ([1], [2]). These results can be viewed as illustrating the significance of the Sabatier principle in heterogenous catalysis.

A rather simple kinetic foundation of “volcano curves” has been proposed a few years ago [3], which can be shown to need only simple bonding parameters to describe the effect of varying the solid catalyst.

I will illustrate the implementation of such a model in the cases of hydrogenation and hydrogenolysis reactions catalysed by transition metals. I will discuss the basic assumptions, the fitting procedures, the physical meaning of the fitted parameters, and the predictions of the models [4].

I will show in which way DFT “bond energy descriptors” should prove useful in the “virtual” pre-screening of putative new catalytic compounds [5].

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[2] R. Chianelli, G. Berhault, P. Raybaud, S. Kasztelan, J. Hafner, H. Toulhoat , “Periodic Trends in Hydrodesulfurization: in support of the Sabatier Principle”, Applied Catalysis A: General **227** (2002) 83.

[3]. Kasztelan, S., Applied Catal. Lett. **83**, (1992) L1-L6.

[4] H. Toulhoat, P. Raybaud, “Kinetic interpretation of catalytic activity patterns based on theoretical chemical descriptors” J. Catal., **216**, (2003) 63.

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3.2 ESF Workshop/Conference Announcements

3.2.1 CECAM/Psi-k SCHOOL and WORKSHOP

Time-Dependent Density-Functional Theory: Prospects and Applications

(http://sophia.ecm.ub.es/2004tddft/2004tddft.htm)

Benasque, Spain, August 29 - September 11, 2004

Organizers: E.K.U. Gross, M.A.L. Marques, F. Nogueira, and A. Rubio

Scientific content:

The use of TDDFT is increasing, and it is fast becoming one of the tools of choice to get accurate and reliable predictions for excited-state properties in solid state physics, chemistry and biophysics. However, in international meetings, schools and workshops, TDDFT has usually been just one of the topics covered. This means that scientists new to the field face difficulties in grasping its many aspects that could be alleviated if they could attend a school on TDDFT. We also believe that a school on TDDFT would be extremely helpful for young graduate students, post-docs and even older scientists that are envisaging a project for which TDDFT would be the tool of choice. For this reason we decided to organize a 10 day school on TDDFT, covering its theoretical, practical, and numerical aspects.

This school will be followed by an international workshop, where the new developments of TDDFT will be discussed. Students attending the Summer School will be encouraged to attend the workshop, so they can get in contact with state of the art research in the field of TDDFT. The purpose of the workshop is to bring together leading experts in the field of TDDFT with different backgrounds, like density functional, many-body, nuclear physics and quantum chemists. This will allow the exchange of ideas between the different fields and the creation of links between the traditionally separated communities. We believe that the intense and informal discussion which is possible in this kind of workshops can contribute to the formation of a strong community in the field of TDDFT. Some of the recent developments of TDDFT that will be covered during the workshop include TDDFT versus current-DFT, van der Waals interactions, applications to biological systems, new functionals, transport phenomena, optical spectra of solids, etc. It will assemble specialists in these and other areas and will consist of several presentations and round-tables.

Location/Timing:

We plan to organize this event at the “Benasque Center for Science” (http://sophia.ecm.ub.es/), Benasque, Spain, from August 29, 2004 to September 11, 2004. Benasque is a beautiful town in the heart of the Pirinees (http://www.benasque.com/). The school will take place from August

29 to September 7, and the workshop will start September 8 and finish on Sep. 12.

Web-site:

Registration and further information can be found in the web site

http://sophia.ecm.ub.es/2004tddft/2004tddft.htm

Tentative program for the school:

The school will be attended by a maximum of around 30 student, and will last 10 days, with theoretical sessions (mostly) in the mornings and practical (tutorial) sessions in the afternoons. The theoretical sessions will consist of two 1.5 hour lectures + 20 minutes for discussion. The practical sessions will last for 3 hours and a computer will be allocated for each two students. This will allow the students to have some time every day for studying and talking to the teachers. The program of the school starts with basic ground-state DFT, then continues with the theoretical and numerical aspects of TDDFT, and will end with an outline of some of its many applications.

A preliminary program of the school can be found in the web page:

(http://sophia.ecm.ub.es/2004tddft/teachers.html)

During the school we will incentive a close and informal contact between the students and the teachers. Furthermore, the students will be stimulated to talk about their current research activities and future interests. We feel that this is an important point, since young scientists should be involved in the building up of a strong community.

Preliminary program of the workshop

The 4 day workshop will take place between the 8-12 September 2004. It will include both invited talks on key aspects of TDDFT (45m each), contributed talks (30m) and a poster session. The tentative list of invited speakers is

Walter Kohn* (Santa Barbara, USA)
Steven G. Louie (Berkeley, USA)
Roberto Car (Princeton, New Jersey, USA)
Rex Godby (York, UK)
Kieron Burke (Rutgers, New Jersey, USA)
Neepa Maitra (Rutgers, New Jersey, USA)
Xavier Lopez (San Sebastian, Spain)
Robert van Leeuwen (Groningen, The Netherlands)
Andreas Goerling (Munich, Germany)
Lucia Reining (Paris, France)
Carla Molteni (Cambridge, UK)
Ursula Roethlisberger* (ETH Zuerich, Switzerland)
Michiel Sprik (Cambridge, UK)
Ulf von Barth (Lund, Sweden)
Carl-Olof Almblahd (Lund, Sweden)
Giovanni Vignale (Univ. Missouri, USA)
Pablo Garcia Gonzalez (UAM, Madrid, Spain)

Massimiliano di Ventra (Virginia, USA)
Juerg Hutter (Zurich, Switzerland)
Risto Nieminen (Helsinki, Finland)
M. Cassida (Grenoble, France)
Yoshi Miyamoto (NEC, Japan)
Martin Fuchs (FHI, Berlin, Germany)
Roy Baer (Naval Res. Lab., Washington DC, USA)
E.K.U Gross (FU Berlin, Germany)

*) Not yet confirmed.

Format of the workshop:

We plan an informal workshop with sufficient time for discussions. The informal character of the talks will be encouraged and presentations which are partly tutorial, given the mixed character of the audience, are most welcome. The time for each talk will be divided into 75the presentation plus 25encouraged to divide their available time into two separate parts if their topic falls under more than one heading.

We will select some posters from the young researchers participating in the workshop to be presented as oral communications.

Participants to the workshop:

The call for participation will be mainly directed to students and scientists specialized on computational physics, quantum chemistry and biophysics. We will limit the number of participants to 60, in order to ensure a maximum interaction between all the scientists participating. Attendance of graduate students and postdocs will be strongly encouraged through the inclusion of short contributed talks and a poster session. Furthermore, we will award to Ph.D. students who present an outstanding poster short oral presentations.

4 General Workshop/Conference Announcements

4.1 Workshop Hands-on-FPLO

First Announcement of the Third Workshop

Hands-on-FPLO

University of California, Davis, June 18 - 22, 2004

FPLO is a highly accurate full potential minimum basis package that solves the Kohn-Sham equations for regular lattices. It comprises scalar relativistic and 4-component relativistic approaches, LSDA and LSDA+U as well as a CPA solver. The workshop is aimed at the exposition of the method, introduction into the algorithms, handling of the package, exchange of experience amongst the users, and introduction to the range of applications. Two previous workshops were held at IFW Dresden, Germany, in 2002 and 2003.

This announcement and further informations are available at:

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

A second (final) announcement will follow in February, 2004.

On behalf of the organizers,

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4.2 ACS PRF Summer School

Time-Dependent Density-Functional Theory and the Dynamics of Complex Systems

Santa Fe, June 5-10, 2004

Time-dependent density-functional theory (TDDFT) was established 20 years ago, and has since then made significant formal and practical progress. Today, TDDFT is the method of choice for calculating excitation energies of complex molecules, and is becoming increasingly popular for describing spectroscopic properties of bulk solids, clusters, and nanostructures. Another growing area of applications is the nonlinear dynamics of strongly excited systems.

This Summer School will provide an in-depth introduction to the fundamental framework of TDDFT, and will give a broad overview of its applications. The School specifically invites students and non-specialists in chemistry, physics and materials science, and will be organized as a 6-day interactive short-course.

The website, including application materials, is at

http://campus.umr.edu/tddft/tddft.htm.

Space is limited.

The organizers are Carsten Ullrich, Kieron Burke, and Giovanni Vignale

4.3 SPRING COLLEGE ON SCIENCE AT THE NANOSCALE

24 May - 11 June 2004

Miramare - Trieste, Italy

The Abdus Salam International Centre for Theoretical Physics (ICTP) is organizing a Spring College on Science at the Nanoscale, to be held at the Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy, from 24 May to 11 June 2004. The College will be directed by Profs.:

Roberto CAR (Princeton University, Princeton,USA),
Supriyo DATTA (Purdue University, West Lafayette, Indiana, USA),
Giacinto SCOLES (SISSA, Trieste and Princeton Univ., USA),
Sandro SCANDOLO (the Abdus Salam ICTP, Trieste).

The Local Organizer will be

Dr. Ralph GEBAUER (the Abdus Salam ICTP, Trieste, Italy).

In recent years it has become possible to manipulate matter at an atomistic scale. The research into ways to perform such manipulations and to carry out measurements, as well as the attempts to understand the basic physics underlying the observed phenomena have rapidly grown into a very active scientific domain. Today, research on nanoscale phenomena is strongly supported in most developed countries due to the important benefits expected from the introduction of nanoscale devices in technological areas such as electronics, micromechanics and biomedicine. But progress in these areas is necessarily linked to advances in the comprehension of the fundamental physical processes taking place at the nanoscale, as well as to cross-disciplinary efforts aimed at unifying languages and concepts from chemistry, materials science and condensed matter physics. In this respect, nanoscale phenomena represent an ideal bench table for the development of new concepts and new trends in basic science.

The field of nanoscience is evolving so rapidly that the gap between achievements in basic research and technological applications has shrunk considerably. It is therefore very desirable to bring researchers from developing countries in contact with this domain of science and stimulate them to be an active part of this field. Making this kind of contact possible is the main target of the Spring College.

The College is planned to focus on three distinct aspects of nanoscience:

(A) Phenomenological aspects
(B) Experimental challenges
(C) Quantum (ab-initio) simulations

About 20-25 world-leading scientists will lecture at the College, covering these domains. Apart from those lectures, introductory tutorials will also be held in order to recall basic concepts underlying the physics at the nanoscale. Hands-on computer exercises and laboratory visits will be offered as supplementary incentives for those interested.

A preliminary list of speakers includes:

Boris Altshuler (Princeton Univ., USA);
Rashid Bashir (Purdue Univ., USA);
Roberto Car (Princeton Univ., USA);
Supriyo Datta ((Purdue Univ., USA);
Julio Fernandez (Columbia Univ., USA);
Cherie Kagan (IBM, USA);
Uzi Landman (Gatech, USA);
Mark Lundstrom (Purdue Univ., USA);
Chris Murray (IBM, USA);
Michele Parrinello (ETH, Switzerland);
Mark Ratner (Northwestern Univ., USA);
Angel Rubio (San Sebastin Univ., Spain);
Matthias Scheffler (FHI Berlin, Germany);
Wolf-Dieter Schneider (EPFL Lausanne, Switzerland);
Giacinto Scoles (Princeton Univ., USA and SISSA, Trieste);
Annabella Selloni (Princeton Univ., USA);
Uri Sivan (Technion, Haifa, Israel);
Erio Tosatti (SISSA, Trieste);
Robert Wolkow (NRC Ottawa, Canada).

Scientists and students from all countries that are members of the UN, UNESCO or IAEA can attend the activity. The main purpose of the Centre is to help researchers from developing countries through a programme of training activities within the framework of international co-operation. However, students, post-doctoral scientists and researchers from developed countries are most welcome to attend. As the College will be conducted in English, participants must have an adequate working knowledge of that language.

As a rule, travel and subsistence expenses of the participants are borne by their home institutions. Every effort should be made by candidates to secure support for their fare (or at least half-fare). However, limited funds are available for some participants who are nationals of, and working in, a developing country, and who are not more than 45 years old. Such support is available only to those attending the entire College. There is no registration fee to attend this activity.

The closing date for the receipt of requests for participation is:

20 February 2004

The Application Form is obtainable from the ICTP WWW server:

`http://agenda.ictp.trieste.it/smr.php?1564`

(which will be constantly up-dated) or from the activity Secretariat (smr1564@ictp.trieste.it).

It should be completed, signed and returned before 20 February 2004 to:

The Abdus Salam International Centre for Theoretical Physics
Spring College on Science at the Nanoscale (smr.1564)
Strada Costiera 11
I-34014 Trieste, Italy

Telephone: +39-040-2240305
E-mail: smr1564@ictp.trieste.it
Telefax: +39-040-224531

`http://agenda.ictp.trieste.it/smr.php?1564`

Trieste, November 2003

Activity's WWW web page:

`http://agenda.ictp.trieste.it/smr.php?1564`

4.4 SNS2004 Conference

7th International Conference on

Spectroscopies in Novel Superconductors (SNS2004)

July 11-16, 2004, Sitges, Spain

With great pleasure we invite you to the 7th International Conference on Spectroscopies in Novel Superconductors (SNS2004) to be held July 11 - 16, 2004 at the Meliá Gran Sitges Hotel in the beautiful coastal town of Sitges near Barcelona, Spain.

SNS2004 continues the successful series of International Conferences held at Argonne (1991), Sendai (1992), Santa Fe (1993), Stanford (1995), Cape Cod (1997) and Chicago (2001). We invite you to explore the SNS2004 Web page at:

http://www.icmm.csic.es/sns2004/

which contains detailed information concerned the Conference, such as Important Dates or Hotel Accommodation.

The First Announcement may be downloaded from

`http://www.icmm.csic.es/sns2004/first_ann.htm`

and also the Registration form is already available in the SNS2004 Web site.

We already sense a very high degree of interest in SNS2004 and expect a large turnout. We recommend that you subscribe to the SNS2004 Mailing List available at the Web site, in order to ensure that you will receive all conference mailings in a timely manner.

Please feel free to forward this message to anyone who you believe would be interested in attending SNS2004.

We expect SNS2004 to be the best SNS yet and look forward to seeing you in Sitges.

Maria C. Asensio
Conference chairperson
LURE, Bat 209D. BP 34
Centre Universitaire Paris Sud
F-91898 Orsay Cedex - France
Tel.: +33 1 6446 8012
Fax: +33 1 6446 4148
http://www.icmm.csic.es/antares/

Arun Bansil
Conference co-chairperson

5 General Job Announcements

Postdoctoral Position in Condensed Matter Theory

Institute of Theoretical Physics,
University of Frankfurt am Main,
Condensed Matter Theory Group

Field(s): computational physics, condensed matter, theoretical physics

Application deadline: Jan 30 (Fri), 2004

Contact: Prof. Roser Valenti

E-mail: openings.valenti@itp.uni-frankfurt.de

Address: Institute of Theoretical Physics, University of Frankfurt am Main

Job description:

Applications are invited for a postdoctoral research position in solid state physics at the Institute of Physics of the University of Frankfurt, Germany. The candidate should have a Ph.D. in theoretical Physics with an excellent academic background and good computational skills. Applicants with research experience on ab initio (Density Functional Theory) calculations on strongly correlated transition metal systems and/or metallorganic materials are encouraged to apply. The focus of the work will be the microscopic description of the behavior of low-dimensional systems by a combination of Density Functional Theory calculations and Many-body methods. Teaching support will be welcomed.

The appointment will be for two years starting in April 2004.

Interested applicants should submit a curriculum vitae and arrange for three letters of reference to be sent to the address below.

Prof. Roser Valenti
Institute of Theoretical Physics
Johann Wolfgang Goethe University
Robert-Mayer-Str. 8
D-60054 Frankfurt am Main
Germany

E-mail:openings.valenti@itp.uni-frankfurt.de

PhD Position in Condensed Matter Theory

Institute of Theoretical Physics, University of Frankfurt am Main, Condensed Matter Theory Group

Field(s): computational physics, condensed matter, theoretical physics

Application deadline: Jan 30 (Fri), 2004

Contact: Prof. Roser Valenti

E-mail: openings.valenti@itp.uni-frankfurt.de

Address: Institute of Theoretical Physics, University of Frankfurt am Main, Condensed Matter Theory Group

Job description:

Applications are invited for a Ph.D. research position in solid state physics at the Institute of Physics of the University of Frankfurt, Germany. The candidate should have a Diplom/M.S. in Physics with an excellent academic background and good computational skills. The focus of the work will be the microscopic description of the behavior of strongly-correlated electron systems by a combination of Density Functional Theory calculations and Many-body methods. Teaching support will be welcomed.

The appointment will be for three years starting in April 2004.

Interested applicants should submit a curriculum vitae and arrange for three letters of reference to be sent to the address below.

Prof. Roser Valenti
Institute of Theoretical Physics
Johann Wolfgang Goethe University
Robert-Mayer-Str. 8
D-60054 Frankfurt am Main
Germany

E-mail:openings.valenti@itp.uni-frankfurt.de

POST DOCTORAL OPENINGS FOR COMPUTATIONAL QUANTUM CHEMISTS/BAND THEORISTS

Chemistry Department, Case Western Reserve University,

Cleveland OH 44106 USA

The above positions are available in the lab of Professor A. B. Anderson. It is desired to begin these projects as soon as possible. The research will center on electron transfer theory and electro-catalytic reaction mechanisms with an emphasis on novel fuel cell electrodes. Both Gaussian and VASP methods will be used and familiarity with both codes would be very desirable.

Please address any questions and make your application to aba@po.cwru.edu. Include your cv with your application and please arrange for three letters of recommendation to be sent. Phone: 216 368 5044; fax 216 368 3006.

Case Western Reserve University is one of several important scientific, cultural, and medical institutions in the University Circle area of Cleveland. If you are not familiar with it, please check it out on the web. Electrochemical research spans several departments at our University and the University is well known for research in this field. The successful candidates will benefit from possible interactions with groups in other departments here and at other universities or at companies.

Case Western Reserve University is an equal opportunity, affirmative action employer and encourages applications from women and minorities.

Postdocoral Position in Computational Materials Science at RICS-AIST

A theoretical postdoc position is open at Research Institute for Computational Sciences (RICS), Institute of Advanced Industrial Science and Technology (AIST) in Tsukuba, Japan. The position is available for three years from 1 April 2004 and funded by the Ministry of Education, Culture, Science, Sports, and Technology (MEXT) of Japan through Grant-in-Aid for Creative Scientific Research (Elucidation and control of interfaces related to organic electronic devices). The focus of the project is to elucidate atomic structures, electronic properties, and chemical reactions at organic/metal interfaces related to organic electronic devices using density functional theoretical (DFT) calculations. It will be carried out in collaboration with Dr. Yoshitada Morikawa (RICS-AIST) and in close contact with experimental groups in Nagoya, Chiba, and Tohoku Universities. A strong background in physics or chemistry, especially, in electronic-structure theory is desirable. Applications including 1) a curriculum vitae, 2) a list of publications and 3) two confidential letters of recommendation or contact information should be addressed to Dr. Yoshitada Morikawa (yoshi.morikawa@aist.go.jp). The evaluation of the candidates begins immediately and will continue until the position is filled.

Additional information:

AIST http://www.aist.go.jp/
RICS http://unit.aist.go.jp/rics/index-e.html

Computing resources at AIST

http://unit.aist.go.jp/tacc/en/system.html

Experimental group of Prof. Kazuhiko Seki at Nagoya University

`http://mat.chem.nagoya-u.ac.jp/info/index_e01.html`

Contact address:

Dr. Yoshitada Morikawa
Research Institute for Computational Sciences (RICS),
National Institute of Advanced Industrial Science and Technology (AIST),
Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8568 JAPAN

Fax: +81-29-861-3171
E-mail: yoshi.morikawa@aist.go.jp
URL: http://staff.aist.go.jp/yoshi.morikawa/

PhD Studentship in Computational Nanotechnology

University College London, UK

We have money from the Interdisciplinary Reserach Collaboration in Nanotechnology for a PhD student (who must be a citizen of an EU country) at UCL in the Condensed Matter and Materials Physics group. Below is a description of the project we have in mind. If you think you might be interested in this project please contact either one of:

Andrew Horsfield a.horsfield@ucl.ac.uk
David Bowler david.bowler@ucl.ac.uk

This project will be a computational study of nanowires both isolated and on semiconductor substrates. We will investigate their structure, both atomic and electronic, at the level of density functional theory, and will study electrical conduction and heat generation in the nanowires using our recently developed time dependent conduction formalism.

The student will be exposed to the phenomenology of nanowires, and more generally to the world of nanotechnology. A very solid grounding in electronic structure methods, notably density functional theory and tight binding, will be provided. Further, the student will be working with state-of-the-art conduction formalisms, and will have the opportunity to contribute new computer code. Links with experiment will be actively sought at all points through the project, both in terms of the conduction properties of nanowires, and their structure and nature on semiconductor surfaces.

Andrew Horsfield
Department of Physics and Astronomy,
University College London,
Gower Street, London WC1E 6BT,
United Kingdom

Phone: +44-(0)20-7679-3500
FAX: +44-(0)20-7679-1360
Email: a.horsfield@ucl.ac.uk

Open position at IRRMA

Post-Doctoral Position at the EPFL (Lausanne)

There is currently a post-doctoral position available for a talented and motivated individual at the Institute for Numerical Research in the Physics of Materials (IRRMA) of the EPFL in Lausanne. The position is for one year and could be extended for a second one. This individual will join a research project in computational condensed matter physics. Research topics concern (i) vitreous materials and (ii) atomic processes at semiconductor-oxide interfaces. Previous experience with computational techniques based on density functional theory is requested. The interested candidates should send their (1) curriculum vitae, (2) publication list, (3) one or two reprints representative of previous research, and (4) confidential letters of recommendation to:

Alfredo Pasquarello
IRRMA-EPFL
PPH-Ecublens
CH-1015 Lausanne
Switzerland
Tel : +41 21 693 44 16
Fax : +41 21 693 66 55
E-mail : Alfredo.Pasquarello@epfl.ch

Refer for more details to the web-page:

http://irrmawww.epfl.ch/G3.html

Position of Assistant-Doctorant at the EPF-Lausanne

The Institute for Numerical Research in the Physics of Materials (IRRMA) at the EPFL in Lausanne is seeking an outstanding PhD student for performing research in the domain of vitreous materials or semiconductor-oxide interfaces (for more details, refer to the web-page:

http://irrmawww.epfl.ch/G3.html)

Typical methods involve first-principles electronic structure calculations and ab initio molecular dynamics simulations. The position, available at the earliest on 1st April 2004, requires a universitary degree in physics or physical chemistry (or equivalent), which should have been obtained by the starting date. The candidate will have teaching duties and shall prepare a doctoral thesis at EPFL. A good background in quantum mechanics and previous experience in FORTRAN programming are required.

The interested candidates should send as soon as possible. their (1) curriculum vitae, (2) the list of passed examinations and relative marks, and (3) confidential letters of recommendation to Prof. Alfredo Pasquarello, IRRMA-EPFL, PPH-Ecublens, CH-1015 Lausanne, Switzerland, Tel. +41/21/6934416, email: Alfredo.Pasquarello@epfl.ch.

POSTDOCTORAL POSITIONS IN NREL'S SOLID STATE THEORY GROUP

IN ALLOY THEORY AND THEORY OF NANOSTRUCTURES

National Renewable Energy Laboratory (NREL)

http://www.sst.nrel.gov

NREL's Solid State Theory Group is looking to fill two Postdoctoral positions. One in the area of Electronic Structure Theory of Semiconductor Nanostructures and one in the area of electronic structure theory of alloys. The work involves developing new methodologies as well as application of our newly developed algorithms. The duration of the positions are up to 3 years. The salary range is $45,000-$55,000 per year, depending on 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 during early 2004 to summer 2004. Applications for both positions 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. Furthermore, the group has outstanding computational facilities: a dedicated local computing system consisting of a 16 node SGI Origin 2000, a 44 processor Linux cluster that will be shortly massively expanded, 4 Sun Ultra 80 workstations and remote access to IBM-SP supercomputers at NREL and NERSC, Berkeley. The group has 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 azunger@nrel.gov.

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

Fellowship available at Isfahan University of Technology, Iran

The computational condensed matter group in physics department of Isfahan University of Technology (IUT) is going to expand its regional scientific activity by acting as an ICTP Affiliated Centre. Following such a mission, the Abdus Salam International Centre for Theoretical Physics (ICTP) and IUT have agreed to support the below mentioned fellowships for the year 2004:

1. Two Fellowship for young researchers (possessing a PhD degree or at the final stages of getting it) from the regional countries (Western South Asia, Central Asia, and Middle East) to come and work in the center as long term visitors (3-6 months).
2. Two Fellowship for senior researchers from the regional countries to come and work in the center as short term visitors (6-12 weeks).

The applicants are expected to have a keen interest in computational condensed matter physics, with some hands on experience on first principle methods.

The fellowships are available from 1st of January 2004.

Interested applicants are requested to send a full CV, a list of publications, a proposal of about 500 words explaining the details of the research project that he/she is going to perform during the stay in the center, the period that he/she wishes to visit the center, and names and addresses (email) of two referees to the following address:

Professor Hadi Akbarzadeh
Department of Physics,
Isfahan University of Technology,
Isfahan, Iran

Email: akbarzad@cc.iut.ac.ir,
Tel: +98-311-3912375 (or 3913700),
Fax: +98-311-3912376.

Accepted candidates are entitled for the following supports:

1. Travel expenses by economy round trip air ticket.
2. Accommodation in IUT Guest House.
3. 400 Euro per month for living expenses (For senior researchers it can be increased to 500 Euro).
4. One full meal per day.

Current research interests of the center Electronic structure calculations, as a valuable tool for understanding the properties of condensed matter, are the main current activity in the computational condensed matter group in physics department of Isfahan University of Technology.

Our calculations are within the density functional theory using FP-LAPW method. We have access and hands on experience to work with WIEN2k code (www.wien2k.at). This general purpose electronic structure code is a very appropriate tool to calculate many properties of a solid: band structure, density of states, equilibrium geometry, magnetic structure, electric-field gradients, hyperfine fields, and X-ray spectra, etc. The code contains LDA+U to study highly correlated systems.

The ongoing research projects in the group are as follow:

1. The effect of pressure and impurity on spin density wave of Cr.
2. First principle study of hyperfine interaction in Cr15X alloys (X= Rh, Cd. Sn, Fe).
3. Ab-initio investigations of magnetic thin films.
4. Structural and electronic properties of matlokite MFX (M=Sr, Ba, Pb; X=Cl, Br, I) compounds.
5. First principles investigation of the bowing parameters in the Mg3xBe3-3xN2 ternary alloy.

Post Doctoral Position in Belfast

There is a Post Doctoral Position available for 35 months in the Atomistic Simulation Group at Queen's University Belfast.

Official Details can be found at

`http://www.qub.ac.uk/jobs/?vac_no=W110&function=view_job`

For Unofficial Details, please contact Tony Paxton (Tony.Paxton@QUB.ac.uk) and see our group's website (http://titus.phy.qub.ac.uk).

The closing date for applications is Friday 30 January 2004.

Positions in Theoretical Surface Science as Research Associate
School of Physics, University of Sydney, Australia

Applications are invited for two Research Associate Positions in the area of computational theoretical surface science in the group of Professor Stampfl in the School of Physics at the University of Sydney, Australia. The research involves development and application of novel ab initio based statistical mechanical schemes for the study of processes and reactions at surfaces; e.g., kinetic Monte Carlo including adparticle interactions via the lattice-gas approach, for calculation of reaction rates in heterogeneous catalysis, or stable and metastable phases in crystal growth. The applicant must hold a Ph.D. in physics, chemistry, or materials science, and have good knowledge of electronic structure theory, and experience in first-principles calculations.

The positions offer good opportunity for international collaborations, and the campus is located near the heart of Sydney. The positions are full-time and fixed term for two years, subject to the completion of a satisfactory mandatory probation period of six months, commencing as soon as possible. Further offers of employment of up to one year may be available, subject to funding and need. For further information, contact Professor Catherine Stampfl on (02) 9351 5901 or e-mail: stampfl@physics.usyd.edu.au or visit: http://www.physics.usyd.edu.au/ stampfl/ To apply, send 5 copies of the application to: The Personnel Officer, College of Sciences and Technology, Carslaw Building, (F07), The University of Sydney, NSW, 2006 by the 14th of February. The application should quote reference number: A01/004499, address the selection criteria, and include a CV, the names, addresses, e-mail, fax and phone number of two referees.

Research Associate Position
Ruhr-Universitaet Bochum, Germany

Applications are invited for a research associate position. The preferred starting date would be spring 2004.

The ideal candidate would have significant experience in electronic structure theory, DFT/MD calculations, surface science, and heterogeneous catalysis. She or he would work primarily on using dynamical (Car-Parrinello) electronic structure methods in order to understand the complex processes involved in chemical reactions occurring at surfaces in contact with dense/hot water. In addition, he/she can also be involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed are accessible via

http://www.theochem.ruhr-uni-bochum.de/go/cprev.html.

The Theoretical Chemistry Group at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references as one pdf/ps file to office@theochem.ruhr-uni-bochum.de.

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
D-44780 Bochum
Germany

Phone : ++49 234 322 6485
Fax : ++49 234 321 4045
office@theochem.ruhr-uni-bochum.de
http://www.theochem.ruhr-uni-bochum.de/

Position: Manager, Materials Science Quantum Application Development

Reports To: Senior Director, Materials Science Research and Development

Location: Cambridge, UK

Advertisement:

Accelrys is the leading provider of software for biologists, chemists, and materials scientists. Through computation, simulation, and the management and mining of scientific data, we accelerate product design, discovery, and development. Our platform technology and consulting services enable enterprise-wide solutions tailored to today's leading research organizations. The result is great science, faster. We are seeking a Manager of Materials Science Quantum Application Development to be part of our dynamic Materials Science Research and Development team.

Summary Job Description

This individual will lead the Materials Science Quantum Application development team in Cambridge, numbering some 4 engineers and scientists. In this role, s/he will provide technical and managerial leadership to a diverse team working on Accelrysb Materials Studio product line: CASTEP, DMol3, and VAMP. S/he will work closely with other Materials Science R&D managers and the marketing organization in defining the requirements and specifications for enhancements to these products. S/he will be responsible for leading and mentoring developers and scientists within the team to ensure the successful enhancement and integration of new technologies within these applications. To achieve this goal, s/he will provide outstanding scientific and technical leadership and will foster a positive and enthusiastic team environment. Responsibilities also include scientific validation studies, tracking and monitoring scientific developments in the area of responsibility, and building and fostering regular contact and research activities with academic groups worldwide.

REQUIREMENTS

The ideal candidate will have both a strong academic record using first-principles atomistic simulations, and experience with commercial-quality software development in both Windows and UNIX/Linux based environments. Additionally, the qualified candidate should possess a PhD in Physics, Chemistry or a related discipline, or the functional equivalent. Intimate familiarity with DFT-based simulations and/or semi-empirical techniques is expected. Significant experience (5+ years) of developing commercial-standard scientific software is required as is experience leading a research or development team. Very good working knowledge of C and FORTRAN 90, and experience of development under UNIX/Linux. OOD, user interface design, and/or

Microsoft Windows skills, including VB, C++, COM, Perl, MFC, are a strong advantage. Very good familiarity with numerical algorithms is expected. The candidate must have prior experience of working with a plane-wave, local orbital and/or semi-empirical code, and the numerical techniques used therein. A strong proven record of successful academic research/development collaborations and ability to coordinate and manage such collaborations is a must as is the demonstrated interpersonal, organizational, and communication excellence.

Should you be available and interested, please send your CV to recruitment@accelrys.com or fax: +44 1223 228501

Position: Senior Software Development Scientist, Quantum Application Development

Reports To: Manager, Quantum Application Development

Location: Cambridge, UK

Advertisement:

Accelrys is the leading provider of software for biologists, chemists, and materials scientists. Through computation, simulation, and the management and mining of scientific data, we accelerate product design, discovery, and development. Our platform technology and consulting services enable enterprise-wide solutions tailored to today's leading research organizations. The result is great science, faster. We are seeking a Senior Software Development Scientist, Quantum Application Development to be part of our dynamic Materials Science Research and Development team.

SUMMARY JOB DESCRIPTION

This individual will be responsible for the scientific development, integration, validation, and maintenance of one or more of Accelrysb flagship quantum-mechanics based scientific application engines within the Materials Studio product line: CASTEP, DMol3, and VAMP. The ideal candidate will have both a strong academic record using first-principles atomistic simulations, and experience with commercial-quality software development in both Windows and UNIX/Linux based environments.

This role involves all aspects of the development and/or integration of new capabilities within these applications, from inception through specification, design, development, implementation, testing, and documentation. The Senior Scientist will work closely with other scientists on the team, as well as marketing, customers, and external academic groups, to define product specifications and scientific algorithms.

REQUIREMENTS

The outstanding candidate will possess a PhD in Physics, Chemistry or a related discipline, or the functional equivalent. Intimate familiarity with DFT-based simulations and/or semi-empirical techniques is expected. Strong academic record with proven experience of developing and applying atomistic simulations using quantum based techniques required. You must have significant experience (3+ years) of developing commercial-standard scientific software. Very good working knowledge of C and FORTRAN 90, and experience of development under UNIX/Linux. Microsoft Windows skills and knowledge of one or more of C++, COM, VB, and Perl are a strong advantage. Very good familiarity with numerical algorithms is expected. Ideally, the candidate has prior experience of working with a plane-wave, local orbital and/or semi-empirical code, and the numerical techniques used therein. Additionally, the ideal candidate will have the ability and willingness to work successfully with a talented team of software developers and scientists, and to follow standard software development best practice. Besides an outstanding and relevant scientific record and good software development skills, the position requires the ability and willingness to work with a diverse team of software engineers and scientists and to adopt commercial software development practices.

Should you be available and interested, please send your CV to recruitment@accelrys.com or fax: +44 1223 228501

Positions (Potentially 5): (Senior) Software Engineers, Materials Science
Reports To: R&D Managers
Location: Cambridge, UK

Accelrys is the leading provider of software for biologists, chemists, and materials scientists. Through computation, simulation, and the management and mining of scientific data, we accelerate product design, discovery, and development. Our platform technology and consulting services enable enterprise-wide solutions tailored to today's leading research organizations. The result is great science, faster. We are seeking 5 enthusiastic (Senior) Software Engineers to be part of our dynamic Materials Science Research and Development team.

Summary Job Description

One position will be responsible for the development of infrastructure components in support of the Materials Studio product line, with particular emphasis on maintenance and enhancement of the client-server infrastructure. Four of the other positions will focus on either the development or maintenance of quantum-mechanics or force-field based scientific applications. All of these positions will be involved in all aspects within the Materials Studio product line, with particular emphasis on the development of the application logic, user interface, and client-server logic. In these roles, you will be involved in all aspects of the development of such components/enhancements, from inception through requirements gathering, specification, design, development, implementation, testing, and documentation. You will work closely with other team members to meet overall product schedules and quality standards, and be capable of independently driving development projects to a successful conclusion.

REQUIREMENTS

The qualified candidates will possess a BS/BA/MS in Computer Science, Engineering, Chemistry or a related discipline or the functional equivalent. You should have experience (3+ years) in commercial software development and a proven track record of successfully delivering complex software development projects. The familiarity with product development life cycle and quality testing assurance methodologies is a must as well as experience with software development skills in both Windows and UNIX/Linux based development environments, including VB, COM, C++, MFC, ATL, STL. Good knowledge of Perl is an advantage, as is a strong background in numerical methods and algorithms. You should have great interpersonal, organizational, and communication skills. A scientific background and knowledge of atomistic modeling is an advantage but not strictly required. Besides excellent technical skills, the position requires enthusiasm, creativity, and the demonstrated ability to develop high-quality software as part of an outstanding team of scientists, developers and software architects. Applications at varying level of seniority/experience will be considered.

Should you be available and interested, please send your CV to recruitment@accelrys.com or fax: +44 1223 228501

PhD Position at the University of Oslo

A doctoral scholarship available to model complex hydrides using density functional calculations in Centre for Materials Science and Nanotechnology at the University of Oslo.

Official Details can be found at

`http://folk.uio.no/ravi/activity/utlysn_hydrogen.rtf`

We seek candidate for the following activity

http://folk.uio.no/ravi/position.htm

For Unofficial Details, please contact

Helmer Fjellvag (helmerf@kjemi.uio.no)

or

P. Ravindran (ponniah.ravindran@kjemi.uio.no)

and see our activities at group's website

http://folk.uio.no/ravi/activities.htm.

The closing date for applications is 1st February 2004.

PhD position
“Quantum Transport through Self-Assembled Metallic Nanowires”

University of Twente, the Netherlands

Project description: On the nanoscale electronic currents are quantum mechanical by nature. Almost perfect nanowires are formed on semiconductor substrates, by depositing Pt atoms on a Ge surface, for instance. These wires are 1 atom in diameter and up to a 1000 atoms long and are ideally suited for studying quantum electronic transport.

In this project we aim to model the relation between transport and structure of such wires. We will use DFT calculations to establish the structure and electronic structure of metal nanowires on semiconductor substrates. For the transport calculations we will extend our recently developed real space quantum scattering approach. We have a strong collaboration with an experimental group, where such nanowires will be made and measured, and interpret their conductance (STM and STS) data. The duration of the project is 4 years, leading to a PhD thesis.

Employment: As PhD student you will be part of the computational materials science group in the physics department of the university of Twente. This group has a substantial program on quantum transport through nanostructures, including topics from spin-electronics and molecular electronics. You will get a contract for 4 years with the FOM foundation (see: www.fom.nl; it is part of the Dutch national science foundation). During the first year the gross salary is 1,668 euro per month. This amount will increase to 2,244 euro during the fourth year.

Information: For more information please contact Dr. G. Brocks (e-mail: g.brocks@tn.utwente.nl, webpage: www.tn.utwente.nl/cms).

Applications: Candidates are invited to submit applications (preferably by e-mail) including a CV, list of university courses followed and grades obtained, and the names and full contact details of 2 referees to:

Dr. G. Brocks, Computational Materials Science, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. E-mail: g.brocks@tn.utwente.nl, Tel: +31 534893155.

Two PhD Positions
“Atomistic Modeling of Lightweight Metal-Hydrides”

Universities of Twente and Nijmegen, the Netherlands

Project description: Lightweight hydrogen storage materials are envisioned to play a central role in a future hydrogen-based economy. This project aims at finding and modeling novel metal-alloys suitable for hydrogen storage, starting from first-principles electronic structure calculations. It is part of the Dutch ACTS program ”Sustainable Hydrogen” in which leading experimental and theoretical groups cooperate.

The project is a cooperation between two groups at the universities of Nijmegen (KUN) and Twente (UT). It involves modeling lightweight metal-alloys plus catalysts from an atomistic point of view using state-of-the-art electronic structure techniques. The central objective is to gain an understanding of the relation between structure and composition of the materials on the one hand, and their thermodynamic, kinetic (UT) and optical (KUN) properties on the other. Frequent interactions with experimental groups within the program are planned. The duration of the project is 4 years, leading to a PhD thesis.

Employment: One Phd student will be embedded in the computational materials science group at the University of Twente, the other in the theoretical physics group at the University of Nijmegen. Both will get a contract for 4 years with the FOM foundation (see: www.fom.nl; it is part of the Dutch national science foundation). During the first year the gross salary is 1,668 euro per month. This amount will increase to 2,244 euro during the fourth year.

Information: For more information please contact Dr. G. Brocks (e-mail: g.brocks@tn.utwente.nl, webpage: www.tn.utwente.nl/cms) or Dr. G.A. de Wijs (e-mail: dewijs@sci.kun.nl).

Applications: Candidates are invited to submit applications (preferably by e-mail) including a CV, list of university courses followed and grades obtained, and the names and full contact details of 2 referees.

For the position in Twente: Dr. G. Brocks, Computational Materials Science, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. E-mail: g.brocks@tn.utwente.nl, Tel: +31 534893155. For the position in Nijmegen: Dr. G.A. de Wijs, ESM, theoretical physics, KUN, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands. E-mail: dewijs@sci.kun.nl, Tel: +31 243652984.

Postdoctoral Position at Berkeley

A postdoctoral position in electronic structure is available at the Department of Physics of the University of California, Berkeley. The initial appointment will be for one year, renewable for a second year.

The position is available immediately, and the review of applications will continue until the position is filled. Interested candidates should contact Ivo Souza via e-mail at isouza@berkeley.edu.

Post-doctoral Position at the Physics Department, Uppsala University, Sweden

The Physics Department at Uppsala University, Sweden is seeking an outstanding post doctoral fellow to perform research on Theory of Materials Properties: ¿From Electronic Structure to Dislocations. Typical methods involve first-principles electronic structure calculations and ab initio molecular dynamics simulations.

The position is available immediately, and the review of applications will continue until the position is filled. The position requires a Ph.D. degree in physics, chemistry or quantum chemistry (or equivalent), which should have been obtained by the starting date. A good experience in FORTRAN and C++ programming is desirable.

The interested candidates should send as soon as possible. their (1) curriculum vitae, (2) list of publications, and (3) confidential letters of recommendation to Professor Olle Eriksson (olle.eriksson@fysik.uu.se) or Associate Professor Rajeev Ahuja (rajeev@fysik.uu.se) at the Department of Physics, Uppsala University, Box 530, 51 21 Uppsala, SWEDEN.

6 Abstracts

Unravelling Orbital Ordering in $La_{0.5}Sr_{1.5}MnO_4$

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Abstract

Orbital ordering (OO) in the layered perovskite $La_{0.5}Sr_{1.5}MnO_4$ has been investigated using the enhanced sensitivity of soft x-ray resonant diffraction at the Mn L edges. The energy dependence of an OO diffraction peak over the $L_{2,3}$ edges is compared to ligand-field calculations allowing a distinction between the influences of Jahn-Teller distortions and spin correlations. The energy dependence of the diffraction peak at the Mn L_1 edge is remarkably different from that observed at the Mn K edge which may be ascribed to the influence of the large $2s$-$3d$ exchange interaction.

(Physical Review Letters, *in print*)
Reprints available from g.vanderlaan@dl.ac.uk

Electron channels in biomolecular nanowires

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Abstract

We report a first-principle study of the electronic and conduction properties of a quadruple-helix guanine wire (G4-wire), a DNA-derivative, with inner potassium ions. The analysis of the electronic structure highlights the presence of energy manifolds that are equivalent to the bands of (semi)conducting materials, and reveals the formation of extended electron channels available for charge transport along the wire. The specific metal-nucleobase interactions affect the electronic properties at the Fermi level, leading the wire to behave as an intrinsically p-doped system.

To be published in: *Journal of Physical Chemistry B* (2004)
Latex and PDF files available from: http://it.arXiv.org/abs/cond-mat/0401012

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Electron channels in biomolecular nanowires

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Abstract

We present a comprehensive first-principles study of the ballistic transport properties of low dimensional nanostructures such as linear chains of atoms (Al, C) and carbon nanotubes in presence of defects. A novel approach is introduced where quantum conductance is computed from the combination of accurate plane-wave electronic structure calculations, the evaluation of the corresponding maximally-localized Wannier functions, and the calculation of transport properties by a real-space Green's function method based on the Landauer formalism. This approach is computationally very efficient, can be straightforwardly implemented as a post-processing step in a standard electronic-structure calculation, and allows to directly link the electronic transport properties of a device to the nature of the chemical bonds, providing insight onto the mechanisms that govern electron flow at the nanoscale.

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Periodic density functional study on structural and vibrational properties of vanadium oxide aggregates

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Abstract

We present periodic density functional calculations within the generalized gradient approximation (Perdew-Wang 91) on structures and vibrational properties of different vanadium oxide aggregates, namely cage type V_4O_{10} and V_8O_{20} gas phase clusters, bulk V_2O_5 and its (001) surface, as well as thin vanadium oxide films supported by α-alumina. Vanadium is differently coordinated by oxygen in the different systems. The calculated vibrational frequencies of bulk V_2O_5 are in good agreement with observed IR and Raman frequencies, for stretching modes the rms deviation is 40 cm^{-1}. The calculations for the V_2O_5(001) surface suggest modifications of previous assignments of HREELS data. In agreement with HREELS, vanadyl frequencies shift to higher wavenumbers on surface formation. The calculated frequencies for bulk Al_2O_3 are systematically lower than the observed IR data (by about 30 cm^{-1}). Models for V_2O_3 supported on Al_2O_3 are obtained when in the outermost layers of Al_2O_3(0001) slabs Al is replaced by V. These films do not show vibrations above 930 cm^{-1}. Oxygen adsorption on top of the vanadium sites on these supported films creates very stable vanadyl groups with binding energies of about 450 kJ/mol ($\frac{1}{2}$ O_2). Bond distances, vibrational frequencies and oxygen binding energies are compared with those of vanadyl groups at the V_2O_5(001) surface and in $(V_2O_5)_n$ clusters. The relevance of the findings for experiments on vanadia particles supported on alumina is discussed.

(submitted to: Phys. Rev. B)

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Anomalous Ferromagnetism of Monatomic Co Wire at the Pt(111) Surface Step Edge

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Abstract

A first-principles investigation of the anomalous ferromagnetism of a quasi-one-dimensional Co chain at the Pt(111) step edge is reported. Our calculations show that the symmetry breaking at the step leads to an easy magnetization axis at an odd angle of ∼20° *towards* the Pt step, in agreement with experiment [P. Gambardella *et al.*, *Nature* **416**, 301 (2002)]. Also, the Co spin and orbital moments become noncollinear, even in the case of a collinear ferromagnetic spin arrangement. A significant enhancement of the Co orbital magnetic moment is achieved when modest electron correlations are treated within LSDA+U calculations.

Paper available from: http://xxx.lanl.gov/abs/cond-mat/0312467
or upon request from A. B. Shick e-mail: shick@fzu.cz

CO adsorption on close-packed transition and noble metal surfaces: Trends from ab-initio calculations

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Abstract

We have studied the trends in CO adsorption on close-packed metal surfaces: Co, Ni, Cu from the 3d row, Ru, Rh, Pd, Ag from the 4d row and Ir, Pt, Au from the 5d row using density functional theory. In particular, we were concerned with the trends in the adsorption energy, the geometry, the vibrational properties and other parameters derived from the electronic structure of the substrate. The influence of specific changes in our setup such as choice of the exchange correlation functional, the choice of pseudopotential and size of the basis set, substrate relaxation has been carefully evaluated. We found that while the geometrical and vibrational properties of the adsorbate-substrate complex are calculated with high accuracy, the adsorption energies calculated with the gradient-corrected Perdew-Wang exchange-correlation energies are overestimated. In addition, the calculations tend to favour adsorption sites with higher coordination, resulting in the prediction of wrong adsorption sites for the Rh, Pt and Cu surfaces (hollow instead of top). The revised Perdew-Burke-Erzernhof functional (RPBE) leads to lower (i.e. more realistic) adsorption energies for transition metals, but to wrong results for noble metals - for Ag and Au endothermic adsorption is predicted. The site preference remains the same. We discuss trends in relation to the electronic structure of the substrate across the Periodic Table, summarizing the state-of-the-art of CO adsorption on close-packed metal surfaces.

J. Physics: Condens. Matter, in print

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Effect of interface bonding on spin-dependent tunneling from the oxidized Co surface

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Abstract

We demonstrate that the factorization of the tunneling transmission into the product of two surface transmission functions and a vacuum decay factor allows one to generalize Jullière's formula and explain the meaning of the "tunneling density of states" in some limiting cases. Using this factorization we calculate spin-dependent tunneling from clean and oxidized fcc Co surfaces through vacuum into Al using the principal-layer Green's function approach. We demonstrate that a monolayer of oxygen on the Co (111) surface creates a spin-filter effect due to the Co-O bonding which produces an additional tunneling barrier in the minority-spin channel. This changes the minority-spin dominated conductance for the clean Co surface into a majority spin dominated conductance for the oxidized Co surface.

(Submitted to Phys. Rev. B; preprint: cond-mat/0308268)

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Kinetic hindrance during the initial oxidation of Pd(100) at ambient pressures

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Abstract

The oxidation of the Pd(100) surface at oxygen pressures in the 10^{-6} to 10^{3} mbar range and temperatures up to 1000 K has been studied *in-situ* by surface x-ray diffraction (SXRD) The results provide direct structural information on the phases present in the surface region and on the kinetics of the oxide formation. Depending on the (T, p) environmental conditions we either observe a thin $(\sqrt{5}\times\sqrt{5})R27^{\circ}$ surface oxide or the growth of a rough, poorly ordered bulk oxide film of PdO predominantly with (001) orientation. By either comparison to the surface phase diagram from first-principles atomistic thermodynamics or by explicit time-resolved measurements we identify a strong kinetic hindrance to the bulk oxide formation even at temperatures as high as 675 K.

(Phys. Rev. Lett. in press (2003))
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7 SCIENTIFIC HIGHLIGHT OF THE MONTH

Density Functional Studies of Molecular Magnets

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Abstract

After a general introduction into the field of molecular magnets the discussion focuses on a more specific discussion of their most important representative species, single-molecule magnets incorporating transition metal ions. We overview traditional model approaches for the phenomenological description of such systems and outline some ways used to parameterize the corresponding models from experiment and from first-principle calculations. The latter can be either multi-determinantal quantum chemical schemes or those based on the density functional theory. In particular we discuss Heisenberg exchange parameters and magnetic anisotropy constants. As a practical example, an introduction into problems and properties of some single-molecule magnets which gained much attention within last years, namely Mn_{12}-acetate, "Fe_8" and "V_{15}" systems, is given. This introduction into systems is followed by a critical comparison of calculation schemes based on the density functional theory that are particularly well suited for the study of molecular magnets. For the above systems we select some benchmark results, obtained by different methods. Finally, we outline our recent progress in the study of other single-molecule magnets, including six-membered "ferric wheels", "ferric stars" and 'Ni$_4$" molecules, which we studied with the use of first-principles methods SIESTA and NRLMOL.

1 Introduction

Following Olivier Kahn[7], who is considered by many as one of the founders of this research topic, *"Molecular magnetism deals with magnetic properties of isolated molecules and/or assemblies of molecules"* (Kahn, 1993). This definition is quite general and there has been recently more emphasis on the aspect of the rational design of molecular magnetic properties in the field (Verdaguer, 2001). Therefore, molecular magnetism is seen *"as a discipline which conceives, realizes, studies, and uses new molecular materials bearing new but predictable magnetic (and other) physical property"* (Linert and Verdaguer, 2003). At present it conveniently hosts many different activities involving methods of physical characterization of matter (optical, X-ray, Mössbauer and neutron spectroscopies, scanning microscopies) and attracts physical models of different degree of sophistication and abstraction. The progress in the field is clearly driven by advances in chemical synthesis of the materials and experiments. However, the combined efforts of physicists and material scientists, particularly theorists, inspires confidence for that such efforts are not only useful for explaining but also for computationally tuning the synthesis of new promising materials. At the moment, the theory dealing with first principles calculations tries to keep the pace with experiment but is still at the stage trying to reproduce the experimental data rather than leading experiment. However, there has been notable progress in the prediction of exchange interactions and magnetic anisotropy energies from density-functional theory during the last few years. In contrast to cases where magnetic exchange interactions follow the famous Goodenough-Kanamori rules (Goodenough, 1955, 1958; Kanamori, 1959), in the case of magnetic anisotropy, another crucial property of molecular magnets, we still have to await similarly clean general insights derived from theory, which could revolutionize the rational design of molecular nanomagnets.

This field of research is very attractive for first-principles microscopic simulations, because the crystal structure of new molecular magnets is well defined, reproducible and is made available rapidly. This is in sharp contrast to the situation in nanoparticle materials or in surface studies where the structure data are usually more ambiguous. Synthetic chemists and theorists performing *ab initio* simulations despite different skills already speak a common language when discussing chemical bonding or magnetic interactions.

Whereas the actual execution of first-principles calculations did not require any special development of basically new numerical schemes, certain difficulties present in and specific to this type of materials provide interesting challenges to computational methods. For example, there are generally a large number of atoms (often several hundreds) in the unit cell, virtual absence of useful crystalline symmetry, and very inhomogeneous spatial distribution of charge density, with "very dense" and "almost empty" regions. The overall progress on the methodological side of atomistic first-principle calculations include more efficient basis sets, new order-N algorithms, along with general augmentation of computational power and this helps to address molecular magnets at a the atomistic level. This task would have been too complicated a decade ago.

The number of materials brought into discussion as molecular magnets is considerable, and some systematics might be appropriate to define better the subject of our present discussion.

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[7] Unfortunately for all of us O. Kahn died the 8th December 1999.

Generally, all materials containing organic building parts and spins associated with unpaired electron(s) fall into one or another category of molecular magnets. Possible classifications may depend on the origin of the unpaired electron(s), the resulting moment localization and mobility, the type of interaction between individual moments, or their spatial organization (weakly coupled molecular fragments; 1-, 2- or 3-dimensional connected structures). A well structured general overview of different classes of molecular magnetic materials can be found in (Molecule-based magnets, 2000).

Magnetic *molecules* contain one or more transition metal centers or rare-earth ions or just organic radicals which are locked at their lattice sites by a careful chemistry of surrounding organic fragments. We won't discuss purely organic magnets where spins are carried by free radicals, although such systems clearly belong to the topic of molecular magnetism, and ferromagnetic ordering with T_c of 35.5 K (Banister *et al.*, 1996) have been demonstrated in them. In the following we restrict ourselves to systems where the spins reside on $3d$ transition metal ions.

In particular we will concentrate on the so-called single molecule magnets (SMM) – see Sessoli *et al.* (1993), – which are often also called molecular nanomagnets. Such materials can often be crystallized, but interactions between the molecular entities remain weak, so that the magnetic behavior probed by experiments is often dominated by intramolecular effects. The discovery of a molecule containing 12 manganese ions $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ with a magnetic ground state of $S=10$ showing a magnetic hysteresis (Sessoli *et al.*, 1993) due to the properties of the single Mn_{12}-molecules have boosted interest in the field enormously. The observed hysteresis in molecular magnets is *not* due to re-magnetization of domains, as in conventional ferromagnets, but reflects the "magnetization tunneling" (Friedman *et al.*, 1996) between quantum states of different m, $-S \leq m \leq S$, of the total spin S of the molecule, as the external magnetic field realigns the degeneracies of different states. This process can only be observed because the relaxation time is very large compared to the measurement time. The relaxation of the magnetization becomes indeed very slow at low temperatures (of the order of several months at 2 K). A single molecule behaves like a single domain and is relatively independent on the magnetization of its neighboring molecules.

What is the present state of art, "figures of merit", perspectives etc. in the field of molecular magnets? The field is becoming rapidly too large to cover all aspects in a compact introduction. There is a number of recent good reviews by Barbara and Gunther (1999); Gatteschi and Sessoli (2003); Verdaguer (2001), along with special issues of journals and conference proceedings (Linert and Verdaguer, 2003; Molecule-based magnets, 2000) which help to access the situation. We single out just several promising directions:

- Single molecule units as "bits" for magnetic storage. The size of molecules of interest is about one order of magnitude smaller than presently accessible domains in magnetic layers, and further miniaturization of conventional domains will be prevented at some point by approaching the superparamagnetic limit. This problem doesn't arise for magnetic molecules, because the *intramolecular* magnetic order is set by the chemistry of a single molecule in question and not due to achieving certain critical size, or certain amount of magnetic atoms. In order to become practicable, this application needs molecules with net ferromagnetic (or ferrimagnetic) intramolecular ordering of sufficient strength (high spin ground state S). The intramolecular magnetic interaction have to be strong enough to prevent decoupling of the spins within the molecule by thermal fluctuations, so that the single molecule effectively behaves like an atom with a giant spin S. Moreover, a high magnetic anisotropy is required, to prevent spontaneous re-orientation of the magnetization of the molecular unit, i.e. to increase its *blocking temperature*. The intrinsic magnetic anisotropy becomes the temperature-determining figure of merit. Weak interactions between adjacent molecules, a prerequisite for writing down magnetic bits independently in each molecule, are usually taken for granted. Potential candidates for such applications, albeit with properties not yet good enough for any real application, are represented by "Mn_{12}-acetate" and "Fe_8" molecules, both with S=10, to be discussed below.

- Working units for quantum computation. This requires a scheme to populate and manipulate excited states of a molecular magnet in a controllable way. Leuenberger and Loss (2001); Leuenberger *et al.* (2003) proposed a seemingly feasibly scheme of imposing a prepared electron spin resonance impulse to write in, transform, and read out the information on a quantum state in the multilevel system of, say, S=10, explicitly referring to two above mentioned systems, "Mn_{12}-acetate" and "Fe_8". A promising technique may make use of the abovementioned magnetization tunneling (Friedman *et al.*, 1996).

- Room-temperature molecule-based permanent magnets, very different in some aspects (solubility in various solvents, biocompatibility) from "conventional" (e.g. intermetallics-based) magnets, and possessing an additional advantage of exhibiting interesting combined magnetooptical and electrooptical properties. Many such systems are based on Prussian blue analogues (Ohkoshi and Hashimoto, 2002; Verdaguer *et al.*, 1999, 2002). Curie temperatures as large as 42 °C (Ferlay *et al.*, 1995), 53 °C (Verdaguer *et al.*, 1999) and 103 °C (Holmes and Girolami, 1999), have been achieved with V, Cr-based Prussian blue analogues. Although such systems can be investigated by first principles calculations without principal problems (see, e.g., Pederson *et al.*, 2002c) and despite the fact that they are generally recognized as molecular magnets, we leave them beyond the current discussion, because they are formed of extended metallorganic patterns Such three-dimensional connectivity is of course essential for obtaining substantial values of T_c.

- Systems which exhibit novel collective phenomena such as magnetism switching by light, temperature, pressure or other physical interactions. Molecules which exhibit spin-crossover behavior would for instance fall into that class. Many such systems are among Fe-binuclear complexes (Gaspar *et al.*, 2003; Ksenofontov *et al.*, 2001a,a). The spin-crossover effects (switching between high-spin and low-spin states in different combinations at two Fe centers) are usually discussed in terms of interplay between intramolecular and intermolecular magnetic interactions, the latter being smaller but not negligible.

2 Structures and properties of some single molecule magnets

Now, in order to make first contact with the materials we are discussing, we review basic structural properties of some examples of the most intensely investigated SMM. From here on we will use Mn_{12}-ac as shorthand for the complete chemical formula $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4 \cdot 2$ $CH_3COOH \cdot$ 4 - H_2O.[8] The Mn_{12}-ac was the first example which showed the slow magnetization relaxation characteristic for a single molecule magnet. This compound is probably the most investigated SMM and, along with the oxo-nuclear iron compound Fe_8, it has shown so far many manifestations of interesting magnetic behavior which keep the research in the field growing. We'll discuss the structure and magnetic properties of these two magnetic molecules in more detail, because one can look at them as kind of test cases the theory was able to explain. For a concise and basic introduction into the field of single molecule magnets we refer the reader to Barbara and Gunther (1999).

2.1 Mn_{12}-ac magnet

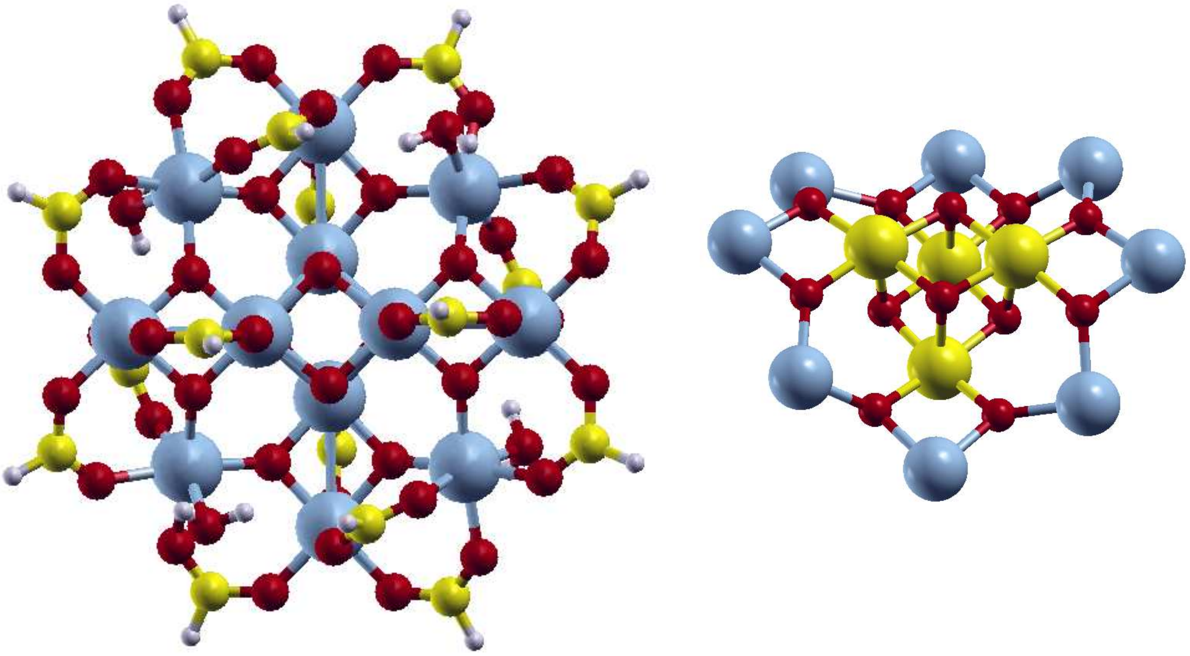

Figure 1: The ball and stick model of Mn_{12}-ac. Left panel: the entire molecule, with methyl groups replaced for clarity by hydrogen atoms (large balls are Mn atoms). Right panel: the magnetic core $Mn_{12}O_{12}$. Eight outer Mn ions have spins $s = 2$ ordered in parallel, four inner $s = 3/2$ are antiparallel to them, resulting in ferrimagnetic structure with total spin $S = 10$.

Mn_{12}-ac has been synthesized and reported in 1980 by Lis (1980). The molecular crystal has tetragonal symmetry with space group $I\overline{4}$, a single Mn_{12}-ac cluster in the crystal posses a S_4 symmetry. Figure 1 shows a ball and stick model of the molecular structure including only some organic ligands. No water of crystallization and acetic acid molecules are included, although they may play an important role, in particular for the process of tunneling of the magnetization. The manganese atoms are six-fold coordinated but show significant Jahn-Teller induced local

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[8] There are now several modification of Mn_{12}-ac known, with different crystal structures, solvent molecules and water coordination – see Gatteschi and Sessoli (2003) for more information. Basically the inner structure of the molecule is always the same, and we'll uniformly refer to all these species as Mn_{12}-ac.

O_h symmetry lowering due to partially filled e_g shells on the outer sites. Right panel of Fig. 1 shows only the magnetic core, for better clarity. The inner four Mn atoms which are in the charge state Mn^{4+} ($s = 3/2$) form, together with four O atoms, a (slightly distorted) cube. The eight outer Mn atoms are in the Mn^{3+} ($s = 2$) charge state. The inner Mn ions are coupled antiferromagnetically to the outer ones, yielding a ferrimagnetic groundstate with a total spin $S = 8 \times 2 - 4 \times 3/2 = 10$. An evidence of the $S = 10$ ground state has been obtained from high field magnetization studies by Caneschi *et al.* (1991) which later has been confirmed by different experimental techniques, such as high field EPR (Barra *et al.*, 1997), high field magnetic torque measurements (Cornia *et al.*, 2000) or neutron scattering (Mirebeau *et al.*, 1999; Robinson *et al.*, 2000).

The (outer) Mn^{3+} ions are distinguishable from manganese atoms in different charge state by the elongated structure of the oxygen atom coordination octahedra or the corresponding oxygen-manganese bond lengths which are typical for Jahn-Teller distortions known in many Mn(III)-systems. This seems to be important for the magnetic anisotropy of the SMM (Gatteschi and Sessoli, 2003).

A surprising feature of the Mn_{12} clusters is that they remain intact in solution. This has been demonstrated by NMR measurements on several derivatives of the material (Eppley *et al.*, 1995). This remarkable finding clearly suggests that the observed magnetic properties have indeed an intramolecular origin. This is further supported by specific heat measurements which found no evidence for long range order in the material (Gomes *et al.*, 1998). Each magnetic molecule in the crystal is well separated from its neighbors by water and acetic acid molecules; Barbara and Gunther (1999) estimate the volume fraction of molecules in crystal to be merely 5%. The critical energy scale for the magnetic behavior is the magnetic anisotropy energy which is of the order of 60 K. The dipole-dipole interaction between molecules is of about 0.03 meV, or 0.35 K, so that one can safely discard it, for practical reasons and for setting up calculations.

2.2 Fe_8 magnet

The octanuclear iron(III) molecular magnet of the chemical formula $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$, with tacn = 1,4,7-trizacyclononane ($C_6N_3H_{15}$), is often referred to as the Fe_8-cluster. The structure the Fe_8-molecular crystal, first synthesized by Wieghardt *et al.* (1984), is shown in Fig. 2. It is acentric $P1$ with $a = 10.52$, $b = 14.05$ and $c = 15.00$Å, $\alpha = 89.90°$, $\beta = 109.65°$ and $\gamma = 109.27°$.

The approximate D_2 symmetry observed in the molecule (Wieghardt *et al.*, 1984) is formally broken by the presence of halide atoms and waters of crystallization. The iron atoms form a structure which is often described as a butterfly. The central iron atoms are connected by oxo-hydroxo bridges to the four outer ones. The large spheres show the iron atoms, which are Fe(III) ions with a d^5 electron configuration. The two inner Fe(III) atoms are coordinated octahedrally to oxygen and the bridging hydroxy ligands. The outer iron atoms are also in octahedral coordination with the corresponding oxy and hydroxy ligands and nitrogen atoms of the tacn-rings. The organic tacn-rings are very important for stabilizing the magnetic core of the molecule because the three pairs of nitrogen dangling bonds complete a quasi six-fold environment for the Fe atoms. Two of the Fe(III) atoms have antiparallel spin projections than

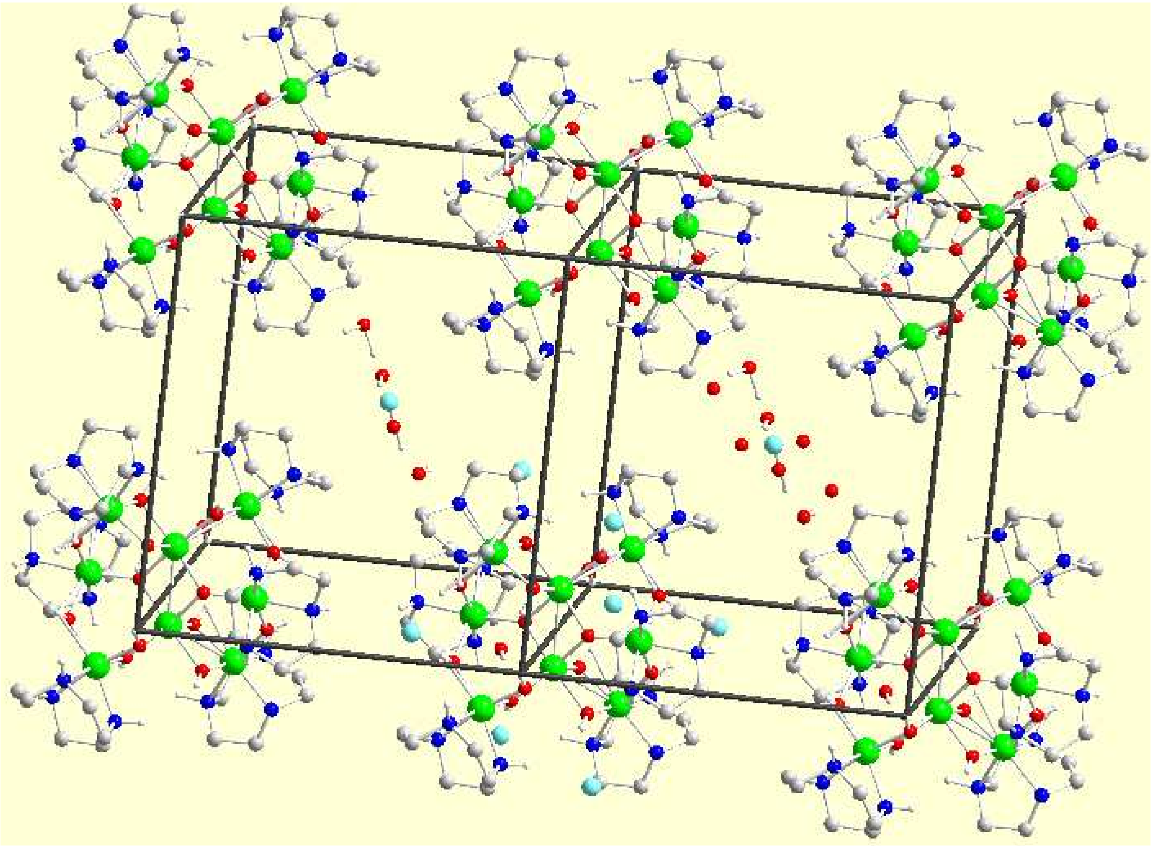

Figure 2: Repeated unit cells of the Fe_8 molecular crystal. Large green balls represent Fe.

the other six, so that the ferrimagnetic coupling of all eight results in the $S = 10$ spin ground state, as was directly proven by polarized neutron scattering measurements (Caciuffo *et al.*, 1998).

The tacn-rings separate the Fe_8-clusters in the crystal, resulting in negligible intermolecular dipole fields which are typically on the order of 0.05T (Wernsdorfer *et al.*, 1999). The resulting formal charge states are nominally Fe^{3+}, $(OH)^{-1}$ O^{-2}, and $tacn^0$, leading to a molecule with an overall formal charge state of +8, which must be compensated by negatively charged halide ions. Due to the lower symmetry as compared to Mn_{12}-ac, the Fe_8-cluster is allowed to have a transverse magnetic anisotropy, which is required in order to observe the quantum tunneling of the magnetization (QTM). This is because the transversal anisotropy is able to couple states with different m_s, that is a basic condition for “real” tunneling processes. In contrast, the tunneling in Mn_{12}-ac is often described as thermally, or phonon assisted, where dipolar and hyperfine interactions playing an important role (Gatteschi and Sessoli, 2003).

One of peculiar features of the Fe_8-cluster making it particularly interesting is that its magnetic relaxation becomes temperature independent below 0.36K, showing for the first time a pure quantum tunneling of the magnetization (Wernsdorfer *et al.*, 1999; Wernsdorfer and Sessoli, 1999). Further, the topological quenching of the tunnel splitting predicted by Garg (1993) has been observed in the form of a periodic dependence of the tunnel splitting on the magnetic field along the hard axis (Wernsdorfer and Sessoli, 1999).

2.3 V_{15} spin system

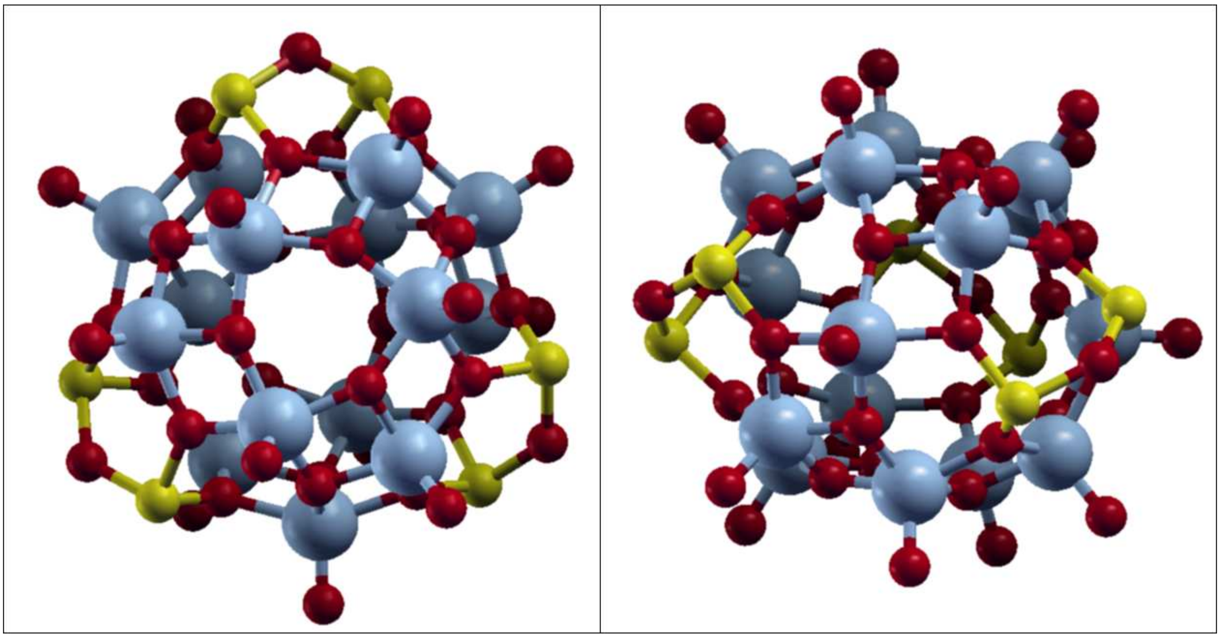

Figure 3: The top view (along the threefold axis, left panel) and the side view (right panel, note the sandwiched structure) to the ball and stick model of the V_{15} spin system. The large balls represent the 15 vanadium atoms. They all contain a single electron in the *d*-shell and couple in complicated ways to yield a total spin ground state configuration of $S = 1/2$.

The $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ molecular crystal was first synthesized by Müller and Döring (1988). The V_{15} molecule comprises spins s=1/2 at all vanadium atoms, which couple together to form a molecule with a total spin S=1/2 ground state. The weakly anisotropic V_{15} demonstrates quantum behavior, such as tunneling splitting of low lying spin states, and is an attractive model system for the study of mesoscopic quantum coherence and processes which destroy it. An understanding of such processes may be of interest for the field of quantum computing. V_{15} has a crystallographically imposed trigonal symmetry with three sets of inequivalent vanadium atoms (Gatteschi *et al.*, 1991). They form two hexagonal layers and an inner triangular layer sandwiched in between. The vanadium atoms are hold in place by oxygens and arsenic atoms so that the complete cluster forms a ball-, or cage-like structure. The empty space inside the cavity is often filled by a randomly oriented water molecule which strictly speaking would formally break the trigonal symmetry.

The unit cell contains two V_{15} clusters and is large enough so that dipolar interactions between them are negligible. Between 20K and 100K the effective paramagnetic moment is 3 μ_B, as for three independent spins, and below 0.5K it changes to the $S = 1/2$ ground state. The experimental results were interpreted with antiferromagnetic interactions between all vanadium atoms (Gatteschi *et al.*, 1991). In order to explain the magnetic behavior, a complicated spin Hamiltonian with many different exchange parameters J_{ij} (as indicated in Figure 4) is required (Kortus *et al.*, 2001a).

Due to the layered structure and the trigonal axis one expects that the V_{15} cluster will show interesting magnetic properties, such as a canted non-collinear magnetic ground state. Calcula-

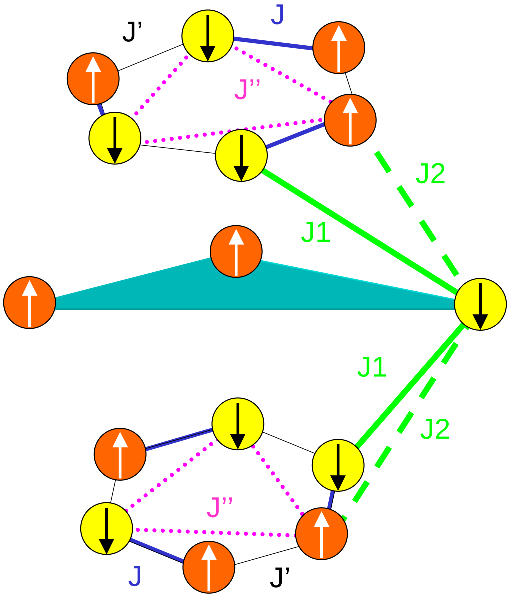

Figure 4: The scheme of different exchange coupling J_{ij} between 15 vanadium atoms needed for the description of the magnetic behavior of that compound. The spin configuration shown is that with the total spin $S = 1/2$, corresponding to the lowest-energy DFT Ising spin configuration.

tions on such correlated systems present a challenge to mean-field frameworks such as density-functional theory, because it is often not possible to construct a single collinear reference state which preserves the inherent symmetry of the system and has the correct spin quantum numbers.

3 Magnetic interactions

A rather complicated and subtle subject that appears often in the discussion of experiments and theory of molecular magnets is that of interatomic magnetic interactions. We begin by introducing a consistent conceptual framework for the following discussion. Later on, we outline several calculation approaches which yielded valuable contribution in the understanding of molecular magnets, and list selected numerical results in their comparison. We conclude by presenting and discussing our new results on several molecular magnet systems of actual interest, that helps to grasp several typical features of electronic structure of this class of materials.

All discussion of magnetic interaction parameters makes sense only in the reference to a particular physical model which in general does not *explain* but *describes* mathematical relations between observables. In particular, the specific character of interaction between spins is not immediately available from calculation nor from experimental measurements. A directly measurable experimental information, like temperature or field dependency of magnetization or magnetic susceptibility, might be more or less satisfactorily fitted on the predictions of a certain model, yielding the values of interaction parameters in the sense of this particular model only. On their side, the first-principles calculations provide the spectrum of eigenvalues, or compare total energy in different magnetic configurations, and derive the estimates of interaction parameters from fitting these data, again, to a particular physical model. Therefore one should be careful in comparing "measured" and "calculated" interaction parameters: they are accessed indirectly and from different starting points, hence their agreement may be accidental, and the source of disagreement not immediately obvious.

3.1 Spin Hamiltonians

The mechanisms of interaction do normally include, as the presumably leading term, the Heisenberg Hamiltonian

$$\mathcal{H} = -2\sum_{i>j} J_{ij}\mathbf{S}_i\mathbf{S}_j\,, \tag{2}$$

with the summation indicates that each pair of spins $\mathbf{S}_i$, $\mathbf{S}_j$ is counted only once. As only the relative orientation of both spins matters, this interaction is isotropic. The dependence on absolute spin orientation, i.e. with respect to the crystal lattice, can be brought in via a modification of the Heisenberg model taking into account anisotropy:

$$\mathcal{H} = -2\sum_{i>j} J_{ij}\left[S_i^z S_j^z + \gamma(S_i^x S_j^x + S_i^y S_j^y)\right]\,. \tag{3}$$

This form of interaction recovers the conventional Heisenberg model in case of γ=1, reduces to the Ising model for γ=0, or to the 2-dimensional interaction for $\gamma \gg 1$. Further on, the single-spin anisotropy can be included, and the Zeeman term added, yielding

$$\mathcal{H} = -2\sum_{i>j} J_{ij}(\mathbf{S}_i\mathbf{S}_j) - D\sum_i(\mathbf{e}_i\mathbf{S}_i)^2 - g\mu_{\mathrm{B}}\sum_i \mathbf{B}\,\mathbf{S}_i\,. \tag{4}$$

The single-spin anisotropy term may lack some of the true physics. It is scaled with its corresponding constant D and depends on the orientation of each spin $\mathbf{S}_i$ relative to a reasonably chosen fixed direction in space $\mathbf{e}_i$; the Zeeman term scales with the external magnetic field B, for the chosen value of the g factor.

It should be noted that the definition of the Heisenberg Hamiltonian in different works differs sometimes in the sign and in the presence of prefactor 2, that must be taken into account when comparing different sets of extracted parameters. The notation as above corresponds to $J > 0$ for ferromagnetic coupling.

A sophistication of such model spin Hamiltonian can be further enhanced by introducing additional parameters, i.e., distinguishing between random (varying from site to site) and constant (global) magnetic anisotropy, yielding the appearance of distinct D parameters in Eq. (4). Moreover, higher-order terms in isotropic interaction (biquadratic exchange, etc.), as well as from antisymmetric Dzyaloshinsky-Moriya spin exchange

$$\mathcal{H}_{\mathrm{DM}} = \sum_{i>j} \mathbf{D}_{ij}\cdot[\mathbf{S}_i\times\mathbf{S}_j]\,, \tag{5}$$

can be introduced. This might be necessary to grasp an essential physics, but makes the extraction of parameters, usually from a limited set of experimental data, more ambiguous, leading to a problem of over-parameterization.

The advantage of *ab initio* approaches to the extraction of interaction parameters is that certain mechanisms of interaction can be switched on and off in a fully controllable way. Thus, all anisotropy terms may only have effect if the spin-orbit interaction is explicitly present in the calculation. The non-collinear orientation of individual spins can sometimes be arbitrarily chosen, and at least different settings of "up" and "down" configurations of spins with respect to a global quantization axis are normally available in any calculation scheme, so that angles between spins become in one or another way directly accessible.

The experiment does not allow such grade of control on the microscopic level; the magnetic field and temperature are eventually the only tunable parameters, and the availability of good-quality oriented monocrystalline samples is not a rule. Microscopic techniques include some (few) spectroscopic studies and (exclusively for Fe-based magnets) Mössbauer effect measurements; which are able, to some extent, to probe charge and spin state of an ion in question.

3.2 Relation to experiment

Once the spin Hamiltonian is agreed on, it can be, at least in principle, diagonalized, and its eigenvalues E_n determine the partition function and all thermodynamic properties in their dependency on magnetic field B and the temperature. Specifically, the molar magnetization is

$$M_{\text{mol}} = -N_{\text{A}} \frac{\sum\limits_n \partial E_n / \partial B \exp(-E_n/kT)}{\sum\limits_n \exp(-E_n/kT)} \tag{6}$$

(N_{A} is the Avogadro number), and the zero-field molar magnetic susceptibility, taking into account the dependence of eigenvalues E_n on the homogeneous magnetic field B_z up to the second order

$$E_n = W_n^{(0)} + B_z W_n^{(1)} + B_z^2 W_n^{(2)} + \dots\,, \tag{7}$$

yields

$$\chi_{\text{mol}} = \mu_0 N_{\text{A}} \frac{\sum\limits_n \left[(W_n^{(1)})^2/kT - 2W_n^{(2)} \right] \exp(-W_n^{(0)}/kT)}{\sum\limits_n \exp(-W_n^{(0)}/kT)}\,. \tag{8}$$

The evaluation of parameter values in the spin Hamiltonian proceeds by fitting thus obtained temperature (and/or magnetic field) dependencies to the measured data. The practical difficulty lies in the diagonalization of the Hamiltonian, whose dimension grows very rapidly with the number of spins and their S values.

A common conceptual difficulty is the necessity to choose between several sets of parameters which yield equally reasonable fit. An example of such ambiguity is given by Katsnelson *et al.* (1999) in fitting the model 8-spin Hamiltonian for Mn$_{12}$-ac to the neutron scattering data.

3.3 Relation to first-principles calculations

In first-principles calculations, one has the freedom to impose certain constraints (fix the magnitude or orientation of magnetization, modify the potential felt by certain electronic states, switch on or off the relativistic effects) and inspect the effect of this on the total energy. Moreover, one-electron eigenvalues and corresponding (Kohn-Sham, or Hartree-Fock) eigenfunctions are also available from a self-consistent calculation.

There are certain subtleties related to the assessment of exchange parameters from quantum chemistry (QC) and in DFT calculations.

In QC one deals with a multi-configurational scheme which allows to mix different spin configurations and to sort out energy eigenvalues corresponding to different total spin values. For two interacting spins $\mathbf{S}_1$, $\mathbf{S}_2$ summing up to $\mathbf{S}' = \mathbf{S}_1 + \mathbf{S}_2$ one gets

$$2\mathbf{S}_1\mathbf{S}_2 = \mathbf{S}'^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2\,,$$

with eigenvalues $[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)]$. For a textbook example $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ this yields a singlet ($S' = 0$) and a triplet ($S' = 1$) states. The corresponding eigenvalues of the Heisenberg Hamiltonian must be then $3/2J$ and $-1/2J$, correspondingly.

Indeed, the basis functions in an *ab initio* calculation are normally pure spin states. In the basis of spin functions $|m_{S_1}m_{S_2}\rangle$, for the case $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ the Heisenberg Hamiltonian takes the form:

$$\begin{array}{c|cccc}
m_{S_1}m_{S_2} & |\,\frac{1}{2}\,\frac{1}{2}\rangle & |{-\frac{1}{2}}\,\frac{1}{2}\rangle & |\,\frac{1}{2}\,{-\frac{1}{2}}\rangle & |{-\frac{1}{2}}\,{-\frac{1}{2}}\rangle \\
\hline
|\,\frac{1}{2}\,\frac{1}{2}\rangle & -J/2 & & & \\
|{-\frac{1}{2}}\,\frac{1}{2}\rangle & & J/2 & -J & \\
|\,\frac{1}{2}\,{-\frac{1}{2}}\rangle & & -J & J/2 & \\
|{-\frac{1}{2}}\,{-\frac{1}{2}}\rangle & & & & -J/2
\end{array} \tag{9}$$

The diagonalization of (9) is achieved by a basis transformation which mixes different m_S values:

$$\begin{array}{lll}
\frac{1}{\sqrt{2}}\left(\,|\,\frac{1}{2}\;{-\frac{1}{2}}\rangle - |\,{-\frac{1}{2}}\;\frac{1}{2}\rangle\,\right) & \text{(singlet)} \quad S=0 & E = \frac{3}{2}J\;; \\[2ex]
\left.\begin{array}{l}
|\,\frac{1}{2}\;\frac{1}{2}\rangle \\
\frac{1}{\sqrt{2}}\left(\,|\,\frac{1}{2}\;{-\frac{1}{2}}\rangle + |\,{-\frac{1}{2}}\;\frac{1}{2}\rangle\,\right) \\
|\,{-\frac{1}{2}}\;{-\frac{1}{2}}\rangle
\end{array}\right\} & \text{(triplet)} \quad S=1 & E = -\frac{1}{2}J\;.
\end{array} \tag{10}$$

In a QC (multi-determinantal) calculation, eigenvalues of singlet and triplet states, E_{S} and E_{T} correspondingly, are immediately accessible. This allows the (formal yet unambiguous) mapping of a first-principles result onto the Heisenberg model:

$$E_{\mathrm{S}} - E_{\mathrm{T}} = 2J\,. \tag{11}$$

The case $S_{1,2} = \frac{1}{2}$ corresponds to, e.g., two interacting Cu^{2+} ions. Other ions from the $3d$ row yield more rich system of eigenvalues – for instance, $S_{1,2} = 1$ (two Ni^{2+} ions) produces a quintet level E_{Q} beyond singlet and triplet, with the energy separation

$$E_{\mathrm{S}} - E_{\mathrm{Q}} = 6J\,. \tag{12}$$

Whether both equations (11) and Eq. (12) can be satisfied by the same J is a measure of validity of the Heisenberg model.

In a DFT calculation, the eigenvalues of multi-determinantal states are not available, and one must rely either on Kohn-Sham eigenvectors or on total energies in specially prepared symmetry-breaking metastable states, subject to different constraints with respect to spin states of a system. In practice, one can try ferromagnetic (FM) or antiferromagnetic (AFM) configurations of two spins, or impose the fixed spin moment (FSM) scheme, first introduced by Schwarz and

Mohn (1984). The total energy in different spin configurations relates *not* to eigenvectors but to diagonal elements of, e.g., the Hamiltonian $\mathcal{H}$ of (9):

$$\begin{aligned} E_{\mathrm{FM}} &= \left\langle \frac{1}{2}\,\frac{1}{2} \right| \mathcal{H} \left| \frac{1}{2}\,\frac{1}{2} \right\rangle = -\frac{1}{2}J\,, \\ E_{\mathrm{AFM}} &= \left\langle -\frac{1}{2}\,\frac{1}{2} \right| \mathcal{H} \left| -\frac{1}{2}\,\frac{1}{2} \right\rangle = \frac{1}{2}J\,, \end{aligned} \tag{13}$$

hence

$$E_{\mathrm{AFM}} - E_{\mathrm{FM}} = J \tag{14}$$

for the above case of $S_{1,2} = \frac{1}{2}$. This is a valid representation for J provided the Heisenberg model itself remains valid throughout the path from FM to AFM state. The latter formula can be approximated using the concept of magnetic transition state (Gubanov and Ellis, 1980). Generally, according to Slater, the shift in the DFT total energy ΔE due to a whatever change Δn_i in the occupation of certain orbitals is

$$\Delta E = \sum_i \Delta n_i \varepsilon_i^* + \mathcal{O}(\Delta n^3)\,, \tag{15}$$

where ε_i^* are Kohn-Sham eigenvalues obtained self-consistently with occupation numbers midway between initial and final states. For the flip from FM to AFM configuration,

$$E_{\mathrm{FM}} - E_{\mathrm{AFM}} \simeq \sum_i \left(n_{i\uparrow}^A - n_{i\downarrow}^A\right)\left(\varepsilon_{i\downarrow}^* - \varepsilon_{i\uparrow}^*\,,\right) \tag{16}$$

where $(n_{i\uparrow}^A - n_{i\downarrow}^A)$ is the magnetic moment (which gets inverted) in the orbital i, and the latter bracket is spin splitting (in energy) of the same orbital, calculated in the configuration with zero spin on atom A (transition state), i.e. induced fully via the interaction with the second spin. While being approximative, the magnetic transition state scheme might have a certain advantage of numerical stability over explicit comparison of large total energy values. Moreover, the result is available from a single calculation and offers a microscopical insight of how different orbitals are affected by magnetic interaction – the information which remains hidden in the total energy numbers. Being of use a number of times in the past (primarily for magnetic oxides), the method was recently applied for the analysis of exchange parameters in Mn_{12}-ac (Zeng *et al.*, 1999).

The validity of either "finite difference" scheme (14), or "differential" procedure (16) presumes that the mapping on the Heisenberg model makes sense, in the first place. However, with just two interacting spins we have no immediate criterion whether this is true. The applicability of the Heisenberg model would mean that the functional part of the interaction comes from the scalar product of two spin operators, with the parameter J_{ij} independent on $\mathbf{S}_i$ and $\mathbf{S}_j$. The mapping on the Heisenberg model may be less ambiguous if done as a limiting case of small deviations from a certain stationary state. The meaning of such deviations in the DFT might be some admixture to pure spin states (in the sense of local spin density functional), i.e., non-diagonal (in the spin space) form of density matrices. It allows a transparent quasi-classical interpretation in terms of non-collinear magnetic density varying from point to point in space – see Sandratskii (1998) for a review. If a pair of local magnetic moments can be reasonably identified in the calculation, and their small variations from the global magnetization axis allowed, the counterparts in the Heisenberg model will be deviations of local exchange fields at two corresponding sites. Matching the leading terms in the angular dependence of interaction energy in the DFT and in the Heisenberg model yields the desired mapping. This line of arguing comes back at least to Oguchi *et al.* (1983) who extracted interaction parameters in simple $3d$ oxides from DFT calculations. Antropov *et al.* (1997); Liechtenstein *et al.* (1987, 1984) worked out closed expression for J_{ij} in a form consistent to spin-fluctuation theories[9] in terms of the elements of the Green's function. When using the final formulae, one should be careful to check whether they don't silently imply $S = 1/2$, and also examine the prefactor and sign which may be introduced differently. The following line of argument leads to the formula which has been applied in a number of calculations. If the total interaction energy of two quasi-classical spins is

$$E = J_{ij}\mathbf{S}_i\mathbf{S}_j \,, \tag{17}$$

its variation by deviating the spins by respective angles $\delta\varphi_i$, $\delta\varphi_j$ reads:

$$\delta^2 E = J_{ij}S^2\delta\varphi_i\delta\varphi_j \,. \tag{18}$$

In the attempt to cast a variation of DFT total energy in a comparable form, one can profit from the Andersen's local force theorem, which works here because we are interested in infinitesimal deviations from the ground state. An explicit derivation of the local force theorem in the desired form is given in an Appendix to the paper by Liechtenstein *et al.* (1987). In terms of the Green's function $\mathcal{G}$ and Kohn-Sham Hamiltonian $\mathcal{H}$ the first variation of the total energy reads

$$\delta E = -\frac{1}{\pi}\int^{\epsilon_{\mathrm{F}}} d\epsilon \,\mathrm{Im}\,\mathrm{Tr}\,(\delta\mathcal{H}\,\mathcal{G}) \tag{19}$$

(which can be shown to be zero), and the second variation

$$\delta^2 E = -\frac{1}{\pi}\int^{\epsilon_{\mathrm{F}}} d\epsilon \,\mathrm{Im}\,\mathrm{Tr}\left(\delta^2\mathcal{H}\,\mathcal{G} + \delta\mathcal{H}\,\mathcal{G}\,\delta\mathcal{H}\,\mathcal{G}\right) \,. \tag{20}$$

The variation of Kohn-Sham Hamiltonian can be explicitly related to rotations in spin space as

$$\delta\mathcal{H} = \frac{i}{2}\delta\varphi_i\,[\mathcal{H},\sigma] \,, \tag{21}$$

with the Hamiltonian composed of spin-dependent part at the site i, with $\Delta_i = V_i^{\uparrow} - V_i^{\downarrow}$ [a potential, in general, non-diagonal in (l,m)] and the rest $\mathcal{H}_0$:

$$\mathcal{H} = \frac{\Delta_i}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \mathcal{H}_0\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \,. \tag{22}$$

This yields for the variation of $\mathcal{H}$

$$\delta\mathcal{H} = \frac{i}{2}\delta\varphi_x\,\Delta_i\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \frac{1}{2}\delta\varphi_y\,\Delta_i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \,. \tag{23}$$

Extracting from Eq. (20) the terms bilinear in $\delta\varphi_i$, recovering cite and spin indexes in the elements of the Green's function G_{σ}^{ij} and implying the summation in (l,m) yields

$$J_{ij} = -\frac{1}{2\pi}\mathrm{Im}\int^{\epsilon_F} d\epsilon\left(\Delta_i G_{\uparrow}^{ij}\Delta_j G_{\downarrow}^{ji} + \Delta_i G_{\downarrow}^{ij}\Delta_j G_{\uparrow}^{ji}\right) \,. \tag{24}$$

---

[9] with magnitude of spin varying, and attributed to J. Note therefore the difference in the definition of J_{ij} between these papers and Eq. (2).

This is the final formula for interaction between isolated spins in otherwise infinite and unperturbed environment. If one is interested in the interaction between two *sublattices* of periodically repeated atom types i and j, the Green function follows explicitly in terms of Kohn-Sham eigenfunctions $\psi^{ilm}_{n\mathbf{k}\sigma}$ and eigenvalues $\epsilon_{n\mathbf{k}\sigma}$

$$G^{ij}_{lm,l'm'}(\epsilon) = \sum_{\mathbf{k}n} \frac{\psi^{*ilm}_{n\mathbf{k}}\psi^{jl'm'}_{n\mathbf{k}}}{\epsilon - \epsilon_{n\mathbf{k}}} \tag{25}$$

and, using for the product of Green's functions

$$\frac{1}{(\epsilon - \epsilon_n)(\epsilon - \epsilon_{n'})} = \frac{1}{\epsilon_n - \epsilon_{n'}}\left(\frac{1}{\epsilon - \epsilon_n} - \frac{1}{\epsilon - \epsilon_{n'}}\right), \tag{26}$$

the integration in energy over occupied states yields

$$J_{ij} = \sum_{\{m\}} \Delta^i_{mm'}\,\chi^{ij}_{mm'm''m'''}\,\Delta^j_{m''m'''} \tag{27}$$

in terms of non-local susceptibility, which depends on Kohn-Sham occupation numbers $n_{n\mathbf{k}\sigma}$,

$$\chi^{ij}_{mm'm''m'''} = \sum_{\mathbf{k}nn'} \frac{n_{n\mathbf{k}\uparrow} - n_{n'\mathbf{k}\downarrow}}{\epsilon_{n\mathbf{k}\uparrow} - \epsilon_{n'\mathbf{k}\downarrow}}\,\psi^{*ilm}_{n\mathbf{k}\uparrow}\psi^{ilm''}_{n\mathbf{k}\uparrow}\,\psi^{ilm'}_{n'\mathbf{k}\downarrow}\psi^{*ilm'''}_{n'\mathbf{k}\downarrow}, \tag{28}$$

– a formula probably first given by Liechtenstein *et al.* (1995) and used in a number of publications, notably by Boukhvalov *et al.* (2002) for Mn_{12}-ac. It should be understood that this formula describes interaction between two sublattices rather than two spins, and hence may give numbers very different from those by Eq. (27). The above derivation relates to $S = 1/2$, therefore the values reported for J_{ij} had to be rescaled according to actual interacting spins on, e.g., Mn atoms, a fact not always clearly stated in publications. Such scaling has been performed using the LDA (fractional) calculated values of magnetic moments, rather than nominal (integer) values.[10]

3.4 Spin-orbit coupling and magnetic anisotropy energy

As early as 1937 van Vleck pointed out that the magnetic anisotropy (MAE) arises mainly because of spin-orbit coupling and other relativistic terms in the Hamiltonian. Calculations of MAE on solids, layered structures and films have been carried out for many years using density-functional theory (Jansen, 1988, 1999; Schneider and Jansen, 2000; Shick *et al.*, 1998; Zhong *et al.*, 1991). Several problems associated with the accurate density-functional-based determination of MAE in the solid state have been identified. For example the role of incomplete orbital polarization has been shown to be one issue related to inaccuracies in the solid; other may be related to correlation effects beyond the mean-field treatment of correlations in the DFT.

Recently, Pederson and Khanna (1999b,c) have developed a method for accounting for second-order anisotropy energies. This method relies on a simple albeit exact method for spin-orbit coupling and a second-order perturbative treatment of the spin Hamiltonian to determine the dependence of the total energy on spin projection. The Cartesian representation of the spin-orbit term is used which is exact and also is more adaptable for multi-center systems:

$$U(\mathbf{r}, \mathbf{p}, \mathbf{S}) = -\frac{1}{2c^2}\mathbf{S}\cdot\mathbf{p}\times\nabla\mathbf{\Phi}(\mathbf{r}). \tag{29}$$

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[10] D. Boukhvalov, private communication.

Using single-particle wavefunctions expressed in terms of a basis set

$$\psi_{is}(\mathbf{r}) = \sum_{j,\sigma} C^{is}_{j\sigma} \phi_j(\mathbf{r}) \chi_\sigma, \tag{30}$$

where the $\phi_j(\mathbf{r})$ are the spatial functions and χ are spin functions, the matrix elements can be expressed as

$$\begin{aligned} U_{j,\sigma,k,\sigma'} &= \langle \phi_j \chi_\sigma \mid U(\mathbf{r}, \mathbf{p}, \mathbf{S}) \mid \phi_k \chi_{\sigma'} \rangle & (31) \\ &= -i \langle \phi_j \mid V_x \mid \phi_k \rangle \langle \chi_\sigma \mid S_x \mid \chi_{\sigma'} \rangle & (32) \end{aligned}$$

where the operator V_x is defined as

$$\langle \phi_j \mid V_x \mid \phi_k \rangle = \frac{1}{2c^2} \left(\left\langle \frac{d\phi_j}{dz} \middle| \Phi \middle| \frac{d\phi_k}{dy} \right\rangle - \left\langle \frac{d\phi_j}{dy} \middle| \Phi \middle| \frac{d\phi_k}{dz} \right\rangle \right). \tag{33}$$

In the above, $\Phi(\mathbf{r})$ is the Coulomb potential. Thus this treatment uses matrix elements of the Coulomb potential with partial derivatives of the basis functions, thereby avoiding the time consuming task of calculating the gradient of the Coulomb potential directly.

Here we generalize some of the derivations from uniaxial symmetry to an arbitrary one. The same definitions and lettering of the symbols is used as by Pederson and Khanna (1999c). In the absence of a magnetic field, the second-order perturbative change to the total energy of a system with arbitrary symmetry can be expressed as

$$\Delta_2 = \sum_{\sigma\sigma'} \sum_{ij} M^{\sigma\sigma'}_{ij} S^{\sigma\sigma'}_i S^{\sigma'\sigma}_j, \tag{34}$$

which is the generalization of Eq. (19) of Pederson and Khanna (1999c). In the above expression, σ sums over the spin degrees of freedom and i, j sums over all the coordinate labels, x, y, z respectively. The matrix elements $S^{\sigma\sigma'}_i = \langle \chi^\sigma | S_i | \chi^{\sigma'} \rangle$ implicitly depend on the axis of quantization. The matrix elements $M^{\sigma\sigma'}_{ij}$ are given by

$$M^{\sigma\sigma'}_{ij} = -\sum_{kl} \frac{\langle \phi_{l\sigma} | V_i | \phi_{k\sigma'} \rangle \langle \phi_{k\sigma'} | V_j | \phi_{l\sigma} \rangle}{\varepsilon_{l\sigma} - \varepsilon_{k\sigma'}}, \tag{35}$$

where $\phi_{l\sigma}$ are occupied and $\phi_{k\sigma'}$ and unoccupied states and ε's are the energy of the corresponding states.

The above equation can be rewritten in a part diagonal in the spin index plus the non-diagonal remainder according to:

$$\Delta_2 = \sum_{ij} \sum_{\sigma} M^{\sigma\sigma}_{ij} S^{\sigma\sigma}_i S^{\sigma\sigma}_j + \sum_{ij} \sum_{\sigma \neq \sigma'} M^{\sigma\sigma'}_{ij} S^{\sigma\sigma'}_i S^{\sigma'\sigma}_j. \tag{36}$$

Using the following relation for the expectation value of a spin operator in a closed shell molecule with excess majority spin electrons ΔN

$$\langle 1 | S_i | 1 \rangle = -\langle 2 | S_i | 2 \rangle = \frac{\langle S_i \rangle}{\Delta N}, \tag{37}$$

the first term of Eq. (36) can be expressed as

$$\sum_{ij} (M^{11}_{ij} + M^{22}_{ij}) \frac{\langle S_i \rangle \langle S_j \rangle}{(\Delta N)^2}. \tag{38}$$

With the help of

$$\begin{aligned}\langle 1|S_i|2\rangle\langle 2|S_j|1\rangle &= \langle 1|S_iS_j|1\rangle - \langle 1|S_i|1\rangle\langle 1|S_j|1\rangle \\ &= \langle 1|S_iS_j|1\rangle - \frac{\langle S_i\rangle\langle S_j\rangle}{(\Delta N)^2}, \end{aligned}\qquad (39)$$

and similar relation for $\langle 2|S_i|1\rangle\langle 1|S_j|2\rangle$, and a bit of algebra the second term of Eq. (36) becomes

$$\sum_{ij} -(M_{ij}^{12} + M_{ij}^{21})\frac{\langle S_i\rangle\langle S_j\rangle}{(\Delta N)^2} + \frac{1}{4}\sum_i M_{ii}^{12} + M_{ii}^{21} \ . \qquad (40)$$

Therefore, the total second order shift Δ_2 together from Eq.(38) and Eq.(40) becomes

$$\begin{aligned}\Delta_2 &= \frac{1}{4}\sum_i M_{ii}^{12} + M_{ii}^{21} + \\ &\quad \sum_{ij}(M_{ij}^{11} + M_{ij}^{22} - M_{ij}^{12} - M_{ij}^{21})\frac{\langle S_i\rangle\langle S_j\rangle}{(\Delta N)^2}. \end{aligned}\qquad (41)$$

As can be easily verified, the last equation gives the same result for uniaxial symmetry as Eq. (21) of Pederson and Khanna (1999c), where the Cartesian off-diagonal M_{ij} matrices vanish and $M_{xx}^{\sigma\sigma'} = M_{yy}^{\sigma\sigma'}$. For the derivation of the above expression of Δ_2 we did not assume any particular symmetry, therefore the resulting expression is general.

In the following, we overview the record of first-principles calculations on some SMM, outline a few typical problems and discuss the achieved results and remaining difficulties.

4 Requirements to a DFT computational scheme; working approaches and levels of accuracy

Physical questions which are of interest in the study of molecular magnets are not basically different from those encountered in the study of magnetism and electronic structure of, say, bulk solids, surfaces, of clusters from first principles in the DFT. One is interested in a description of the ground-state electronic structure and, as far as possible, of lowest excitations, in terms of Kohn-Sham eigenvalues and corresponding charge and spin density. It is advantageous to have access to sufficiently accurate total energies for comparing different competing charge or spin configurations; moreover, forces could be needed to perform conjugate-gradient structure optimization, or simulation of vibrations. These requirements are quite common in the practice of DFT calculations. The simulation of molecular magnets presents, however, certain technical difficulties which are not necessary typical for all DFT applications, and impose limitations both on the choice of calculation code for an efficient use and on the number of systems addressed so far in a first-principle simulations. These difficulties are:

1. Large number of atoms, up to several hundreds of atoms per repeated structural unit.
2. Low space group (or, point group) symmetry – or none at all, that does not allow the methods which use (l,m)-expansions in lattice harmonics (KKR, FLAPW) to profit from efficient block diagonalization.

3. Typically large size of a simulation box and, on the average, low density of atoms, that makes planewave methods with a global basis set cutoff inefficient.

4. The presence of transition-metal, or even rare earth, atoms with deep core states and, sometimes, with important semicore, along with the rest of predominantly light organic atoms. This might create difficulties for the use of norm-conserving pseudopotentials.

5. In tight-binding methods with fixed basis sets, specific problems may arise due to the need to tune and optimize the basis, as charge configurations and spatial distribution of density in molecular magnets may differ from those one is acquainted with in crystalline compounds.

6. The lack of energy dispersion (due to very week coupling between molecular units) and quite commonly a dense spectrum of nearly degenerate discrete states in the vicinity of HOMO-LUMO gap, which makes the self-consistency slowly convergent or even unstable.

Retrospectively, it seems understandable that larger number of calculations done so far employed one or another scheme using flexible tight-binding bases. Pseudopotential planewave calculations are not much represented, although one may expect an increase of their fraction, particularly with the use of ultrasoft pseudopotentials, in the future. Other all-electron methods (FLAPW) were used only for benchmark calculations on simplified systems. One can also anticipate a certain impact of basis-free, purely numerical approaches in the future.

In the following we critically compare several families of methods which played, or are expected to play, an important role in DFT calculations on molecular magnets, and emphasize several representative results.

4.1 Tight-binding linear muffin-tin orbital methods

The **tight-binding linear muffin-tin orbitals** (TBLMTO – Andersen and Jepsen, 1984; Andersen *et al.*, 1987; TBLMTO homepage) method has been used by the Ekaterinburg group for calculations of electronic structure and interaction parameters of Mn_{12}-ac (Boukhvalov *et al.*, 2002) and V_{15} (Boukhvalov *et al.*, 2003). The calculation method used in these works was indeed TB-LMTO and not the LMTO method in the less accurate "orthogonal approximation" (Gunnarsson *et al.*, 1983) as erroneously cited in these publications.[11] The calculation used real (tetragonal) structure of molecular crystal and periodic boundary conditions. The interatomic exchange parameters J were estimated along Eq. (27,28).

Having the advantage of compact and flexible (numerical and adjustable in the course of calculation) basis set, the LMTO method faces difficulties in the treatment of loosely packed structures, as it employs space filling by atomic spheres and/or "empty spheres" – in crystals with large and low-symmetric cavities, a cumbersome and ambiguous procedure. There are further drawbacks of LMTO for the treatment of molecular magnets. First, the method always employs periodic boundary conditions, so that molecular units must be posed either in their true (and very diffuse) crystalline arrangement, or – in order to simulate them as as isolated entities – with substantially

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[11] D. Boukhvalov, private communication

enlarged lattice parameters. Second, the method has limitation of only one principal quantum number per l value in the basis set, i.e., $3p$ and $4p$ states cannot be simultaneously present in the valence band. These deficiencies are known to degrade delicate results of calculation, such as placement of some bands, or their dispersion in solids. Therefore one should access the quantitative results of these LMTO calculations with care. Possible indications of inferior numerical accuracy are the total magnetic moment of the Mn_{12}-ac system which is 19 μ_{B} in the LDA, at variance with experiment and other calculations (Pederson and Khanna, 1999a,b,c; Zeng *et al.*, 1999), yielding 20 μ_{B}, as well as the absence of HOMO-LUMO gap in both Mn_{12}-ac and V_{15}, again in variance with calculations by different methods. One should note, however, that the overall shape of local DOS is consistent with results of other calculations.

Boukhvalov *et al.* emphasize the importance of intraatomic correlation in the description of magnetic interactions and excitation spectra of Mn_{12}-ac and V_{15}. This might well make sense as evidenced by rich experience to this subject with manganites and vanadates, where the local coordination of transition metal ions and electronic structure are somehow similar to those in molecular magnets. The intraatomic correlation may be brought into the calculation by means of the LDA+U approach (Anisimov *et al.*, 1997), and depending on the *ad hoc* choice of average Coulomb parameter U. There are certain arguments for the choice of this parameter in the papers cited, U=4 eV for V_{15} and U=8 eV for Mn_{12}-ac. Not less important than the actual results with these parameter values are the trends with U varying, which have been reported for Mn_{12}-ac. One finds that as U changes from 4 to 6 to 8 eV, the exchange interaction parameters between four inner Mn atoms of the cubane core vary from 37 to 33 to 30 K (other Mn–Mn interaction constants, of the same order of magnitude, change in a similar manner). Moreover, local magnetic moments on all Mn atoms get slightly enhanced, and the band gap increases from 1.35 to 1.78 to 2.01 eV. This trends follow from a qualitatively transparent fact that higher U values deepen in energy the occupied $3d$ states and plunge the unoccupied, thus increasing the band gap. As the spin-flip excitations across the gap become more difficult, and they contribute to nonlocal susceptibilities (the denominator in Eq. (28) increases), this has an effect of reducing the interatomic exchange interaction. This mechanism will further be discussed in Section 5.

4.2 Gaussian-type orbital methods: NRLMOL

• The linear combination of atomic orbitals method with a basis of **Gaussian-type orbitals**, of which several “flavors” are known and have been in use.

This approach is “full-potential” one in the sense that no muffin-tin or atomic spheres geometry is imposed, and the spatial form of potential is fairly general. In particular the version implemented in the Naval Research Laboratory Molecular Orbital Library (NRLMOL) code (Jackson and Pederson, 1990; NRLMOL homepage; Pederson and Jackson, 1990) has been frequently used in calculations on molecular magnets.

The NRLMOL program package developed by Pederson, Jackson and Porezag is an all-electron Gaussian-type orbital implementation of DFT (Briley *et al.*, 1998; Jackson and Pederson, 1990; Pederson and Jackson, 1990, 1991; Pederson *et al.*, 1988; Pederson and Lin, 1987; Pederson *et al.*, 2000c; Porezag and Pederson, 1999, 1996; Quong *et al.*, 1993). It has been applied successfully to calculate the electronic and magnetic properties of several molecular nanomagnets (Baruah and Pederson, 2002, 2003; Bobadova-Parvanova *et al.*, 2002; Kortus *et al.*, 2002a,b, 2001a,b; Kortus and Pederson, 2000; Kortus *et al.*, 2002c; Pederson *et al.*, 2002a; Pederson and Khanna, 1999a,b; Pederson *et al.*, 2000a, 2002b, 2000b). By including the spin-orbit coupling it is possible to calculate the magnetic anisotropy energy, which is a crucial parameter for understanding the magnetic behavior of SMM. The agreement between experiment and the result from the first-principles calculation is in many cases surprisingly good. Therefore it seems to be suitable to give some details on this particular numerical implementation.

The molecular orbitals were expanded as linear combinations of Gaussian functions centered at the atomic sites; multicenter integrals are evaluated numerically on a specially generated variational integration mesh – see Pederson and Jackson (1990) for details. An efficient parallelization (Pederson *et al.*, 2000c) makes all-electron calculations with more than hundred atoms feasible in affordable time, a prerequisite for useful applications in the domain of SMM. The problem of basis optimization, severe one in all methods employing localized and fixed basis functions, is solved in NRLMOL by tuning to the solutions of self-consistent isolated atoms (Porezag and Pederson, 1999).

Self-consistent potentials, obtained numerically, are least-square fitted to the sum of bare spherical Gaussians or Gaussian-screened $1/r$ potentials, in order to facilitate multicenter integrations.

Given the basis sets and the Gaussian-representation of the atomic potentials, it is possible to obtain very good insight into the class of multicenter integrands that need to be integrated, and this information is used to generate a numerical variational integration mesh (Pederson and Jackson, 1990) that allows to precisely determine integrals required for calculation of secular matrices, total energies and derivatives according to:

$$I = \int \mathrm{d}\mathbf{r} Q(\mathbf{r}) = \sum_i Q(\mathbf{r}_i)\Omega_i \,, \tag{42}$$

where Ω_i is the volume associated with point $\mathbf{r}_i$. Errors arising from the numerical integration can easily be checked and controlled by adjusting a few parameters which control the mesh construction. It should be emphasized that the Gaussian-screened potential are only used to optimize the numerical quadrature schemes used for mesh generation.

Once self-consistency is achieved the forces acting on each atom are determined from the Hellmann-Feynman-Pulay theorem (Feynman, 1939; Hellmann, 1937; Pulay, 1969). After obtaining all the forces acting on all the atoms a conjugate-gradient method, or other force-based algorithms, can be used to carry out geometry optimizations. Once the equilibrium geometry and Kohn-Sham wavefunctions is obtained, the properties available for the analysis include (beyond the standard set provided by any DFT package) polarizabilities, vibrational frequencies, infrared and Raman spectra and magnetic anisotropy energies.

For the $[\mathrm{Mn_4O_3Cl_4(O_2CCH_2CH_3)_3(NC_5H_5)_3}]$ system, containing as its core a $\mathrm{Mn_3^{3+}Mn^{4+}}$ pyramid and possessing a magnetic moment of 9 μ_B per unit ($\mathrm{Mn^{3+}}$ spins are anti-ferromagnetically coupled to $\mathrm{Mn^{4+}}$), Park, Pederson and Bernstein (2003) calculated the properties related to dimerization. The $\mathrm{Mn_4}$ units were presumed to couple antiferromagnetically, based on their unusual quantum tunneling properties (Wernsdorfer *et al.*, 2002), that was now confirmed in a calculation by NRLMOL (Park *et al.*, 2003c). A fit to the Ising model yields intraatomic exchange parameters of 44 K (ferromagnetic; $\mathrm{Mn_3^{3+}}$–$\mathrm{Mn^{3+}}$) and -152 K (antiferromagnetic;

Mn_3^{3+}–Mn^{4+}) – both overestimated by roughly a factor of two in comparison with experiment-derived values. The intermolecular coupling of merely -0.24 K is also twice larger than the experimental fit value. In addition to structure relaxation, Park *et al.* performed a calculation of vibration spectra with infrared and Raman intensities – the data not yet available from experiment but extremely important for identification and further characterization of this molecular magnet.

4.3 Numerical atom-centered basis functions : Siesta

The SIESTA method and computational code (SIESTA homepage; Soler *et al.*, 2002) also uses compact atom-centered basis functions, but (differently from NRLMOL) numerical ones with strict spatial confinement, as the most frequent choice. (Gaussian-type orbitals, or other fixed functions at the user's convenience, are equally available for the basis set). Due to strict confinement of basis functions, the program can make a clean distinction between cases of isolated fragment (molecule or cluster), "chain", "slab" or "crystal" cases (with periodic boundary conditions in one, two or three dimensions, correspondingly), and to correctly construct Madelung terms according to each case. Keeping trace on local neighborhood in the calculation of matrix elements, in combination with order-N facilities (see, e.g., Ordejón, 1998; Sánchez-Portal *et al.*, 1997), makes SIESTA a great method for treating large low-coordination low-symmetry structures, as molecular magnets exactly are. In contrast to NRLMOL which determines the coulomb and exchange-correlation potentials analytically from the Gaussian representation of the wavefunctions, SIESTA employs fast Fourier transform of the residual charge density (after subtraction of dominant atom-centered contributions) for the solution of the Poisson equation, that also yields high (and controllable) accuracy needed especially in the calculation of forces and optimization of structure. Moreover, for periodic systems (as molecular magnets generally are, in a crystalline state) the components of stress tensor are calculated, and can be used for simultaneous optimization of lattice parameters and internal coordinates subject to target pressure. Particularly important for magnetic systems is the option of treating "non-collinear" (i.e., not diagonal in the spin space) density matrix, that allows to simulate deviations of local magnetic moments from the global magnetic axis – for a recent application, see Postnikov *et al.* (2003b). Differently from two above discussed methods, SIESTA is not all-electron one but employs norm-conserving pseudopotentials (Troullier and Martins, 1991, among other choices) and allows to apply the core correction after Louie *et al.* (1982). As the basis set is of localized functions and not planewaves, the use of hard pseudopotentials, like those of transition metals (also "small core", with semicore states attributed to the valence band) or oxygen, is not problematic. SIESTA was designed in view of large distorted systems and dynamical simulations therein, so that properties of space group (or point group) symmetry are essentially lost. Therefore no special treatment of symmetrized molecular orbitals is provided.

As with other pseudopotential methods SIESTA in its present version requires some care in choosing and testing pseudopotentials prior to calculation, and, moreover, in choosing basis orbitals. A certain freedom in the tuning of the latter is more matter of experience than of consistent control in a variational procedure (as is the case with planewave cutoff). Whereas being, as a rule, reasonably workable, such settings are difficult to consistently improve. More insight in the problem of basis sets was provided by Sánchez-Portal *et al.* (1996) and Junquera *et al.* (2001).

The application of Siesta to molecular magnets is relatively new. We outline some recent results below.

4.4 Discrete variational method

The **discrete variational method** (DVM) (Painter and Ellis, 1970; Rosen *et al.*, 1976), one of earliest DFT schemes to find applications in chemistry, seems to be potentially very well suited for the studies on molecular magnets. The method is all-electron one, it uses basis of numerical atomic orbitals, and the 3-dimensional integration over the space outside the spheres circumscribing core regions of each atom is done on a pseudorandom numerical grid. DVM was used in one of the first *ab initio* calculations of electronic structure of the Mn_{12}-acetate (Zeng *et al.*, 1999). Apart from discussing charge states, magnetic moments and local DOS of three distinct groups of Mn and O atoms in the molecule, which largely remained uncontested by subsequent calculations, Zeng *et al.* estimated Heisenberg exchange parameters in the magnetic transition state scheme (Gubanov and Ellis, 1980), an extension of Slater's original transition state *ansatz*, through a procedure outlined above in Sec. 3. Flipping the spin at one atom and detecting the shift of the $3d$-energy level on another one due to induced magnetic polarization helps to arrive at a system of equations where different interatomic exchange parameters are coupled. For the sake of simplicity and the clearness of analysis, only collective (non-symmetry-breaking) spin flips on all atoms belonging to each set of Mn atoms, – Mn(1) in the inner cubane, Mn(2) and Mn(3) in the peripheral region, see Fig. 1, – were allowed in the analysis of Zeng *et al.*. This means that four spins within each group always remained rigidly ferromagnetically coupled. It resulted in a system of three equations, whence the values of J_{12}, J_{23} and J_{13} could have been determined. The DFT results were explicitly fitted to the Heisenberg Hamiltonian of the form of Eq. (2). However, the parameters J_{11} etc., representing the coupling within each group, did not appear in the fit, because the spin excitations necessary to probe them, which would break the symmetry of the molecule, were not allowed. Their inclusion in an otherwise organized calculation could result in renormalization of exchange parameters.

The values of J_{12}, J_{23} and J_{13} are given in Table 1; they are all negative, i.e. indicate an AFM coupling (as could be expected due to a more-than-90° superexchange pathway through bridging oxygens), and hence frustration in accommodating three spin subsets.

4.5 Planwave methods

The use of **planewave** basis for calculation on molecules is, as was mentioned above, computationally inefficient, but technically feasible and, with sufficiently high cutoff, also ultimately accurate. Massobrio and Ruiz (2003) recently compared straightforward (from the total energy difference in low-spin and high-spin configuration) estimates of Heisenberg-model exchange parameters J for several Cu-based binuclear molecules: $\mathrm{Cu_2(CH_3COO)_4}$, $[\mathrm{Cu_2(\mu\text{-}OH)_2(bipyrimidine)_2](NO_3)_2{\cdot}4H_2O}$ and $[(dpt)\mathrm{Cu}(\mu\text{-}\mathrm{Cl})_2\mathrm{Cu}(dpt)]\mathrm{Cl_2}$ (dpt = dipropylenetriamine), using identical norm-conserving pseudopotentials and exchange-correlation scheme (among other,

Table 1: Electronic structure parameters of Mn_{12} from *ab initio* calculations.

Method	Magnetic moments (μ_B)			Heisenberg exchange parameters (K)		
	Mn(1)	Mn(2)	Mn(3)	J_{12}	J_{13}	J_{23}
DVM[a]	3.056	−3.889	−4.039	−136	−72	−102
NRLMOL[b]	2.57	−3.63	−3.58	−57	−41	−8
LMTO[c], U=4 eV	2.72	−3.44	−3.65	−53	−47	−19
LMTO[c], U=8 eV	2.92	−3.52	−3.84	−47	−26	−7

[a] Zeng *et al.* (1999); LDA.

[b] Pederson and Khanna (1999c); GGA; moments within a sphere of 2.5 Bohr. J values by Park *et al.* (2003b).

[c] Boukhvalov *et al.* (2002); LDA+U; moments within spheres of 2.7/2.8 Bohr (inner/outer Mn atoms).

differing options) as with Gaussian-type basis functions. The largest system consisted of 62 atoms, a moderate number by the standards of a calculation with localized basis functions. For the computational load with the planewave basis, however, it is the size of the simulation box that primarily matters. Here its linear size of 18.5 Å resulted in about $2.4{\cdot}10^6$ plane waves for the expansion of charge density and demanded hours of highly parallelized execution. The small values of J obtained in the plane-wave calculation (−518, −95 and +61 cm^{-1}, correspondingly) were of correct correct sign and order of magnitude in all cases, although deviations in absolute value, from experimental estimate and between different exchange-correlation flavors, were up to 50%.

5 Some recent developments

In the following we outline some recent results on relatively “new” molecular magnets, i.e. systems which have only become available during the last few years, For the study of their electronic characteristics several questions arose which our calculations attempted to clarify. “Ferric wheels” gained interest, not in the last place, because of their “esthetically rewarding” (Gatteschi and Pardi, 2003) shape. Two examples discussed below have an AFM ground state; consequently they might find applications related to quantum tunneling and quantum computing. Other structurally similar (although chemically different) examples include 3*d* ions (notably Mn) at larger distances, with magnetic interactions mediated by organic radical groups that lead to strong antiferromagnetic couplings of Mn ions. An example is the molecule $[Mn(hfac)_2(NITPh)]_6$ (hfac= hexafluoroacetylacetonate, NITPh= 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-oxide), see Gatteschi and Pardi (2003) with a net spin of S=12. “Ferric stars” include a central 3*d* ion to which peripheric ions couple antiferromagnetically which results in a net spin value in the ground state. Due to their not-negligible magnetic anisotropy these systems look like possible prototypes for magnetic storage. Ni_4 is a seemingly simple magnetic molecule for which a fit of experimental data of magnetization vs. magnetic field to the

Heisenberg model fails quite dramatically, and possible reasons for deviation have been studied, with the help of first-principles calculations. Finally, we consider a two-nuclei model system with the aim to study the effect of intraatomic correlation ("Hubbard U") on the electronic structure and interatomic magnetic interactions in a more numerically accurate calculation than has yet been accomplished (for Mn_{12} by TB-LMTO, Boukhvalov *et al.*). In the most recent case the calculations have been performed with the FLAPW method (FLEUR homepage), for other systems – by methods using atom-centered localized basis functions, either SIESTA or NRLMOL.

5.1 "Ferric wheels"

Hexanuclear "ferric wheels" $M\mathrm{Fe}_6[\mathrm{N}(\mathrm{CH}_2\mathrm{CH}_2\mathrm{O})_3]_6\mathrm{Cl}$ (M = Li, Na, see Fig. 5), the systems to be discussed below, were synthesized at the Institut für Organische Chemie in Erlangen (Saalfrank *et al.*, 1997) and labeled as substances **4** and **3** in the latter publication. There exist a large family of ferric wheels with a different even number ($N = 6, 8, 10, 12, 18$) of iron atoms (Abbati *et al.*, 1997; Caneschi *et al.*, 1996, 1999, 1995; Pilawa *et al.*, 1997; Saalfrank *et al.*, 1997; Taft *et al.*, 1994; Taft and Lippard, 1990; Waldmann *et al.*, 2001, 1999; Watton *et al.*, 1997). Besides the ferric ones, there have been reports on wheels with other transition metal ions such as an eight membered Cr(III) wheel (van Slageren *et al.*, 2002), a Cu(II) (Lascialfari *et al.*, 2000; Rentschler *et al.*, 1996), a Co(II) (Brechin *et al.*, 2002), a Mn(II) (Abbati *et al.*, 1998) and a 24 membered Ni(II) wheel (Dearden *et al.*, 2001). The latter structure contains the largest so far number of transition metal ions in a wheel-like structure. Synthesis of odd-numbered magnetic wheels or necklesses appears to be a nontrivial task.

Fe atoms in these compounds are connected by oxo-bridges, that are reminescent of the 90° coupling of magnetic atoms in transition-metal oxides. The nearest coordination of the Fe atom is octahedral; two pairs of O ions form bridges to the neighboring Fe atoms on both sides; the fifth oxygen (referred to below as "apical") and the nitrogen ion are connected by the C_2H_4 group. The octahedra are slightly distorted, to accommodate the stiffness of oxo-bridges with the curvature of the molecular backbone. While the Fe–O–Fe angles differ slightly in the Li-centered and Na-centered wheels (101.1° and 103.3°, respectively), the structure of the two molecules is almost identical.

According to magnetization and torque measurements by Waldmann *et al.* (1999), these systems are characterized by S=5/2 on the Fe site, thus implying a highly ionized Fe(III) state. Moreover, a fit to the spin Hamiltonian of the Heisenberg model (2) yields the J values of -18 to -20 K for the Li-wheel (depending on sample and method) and -22.5 to -25 K for the Na-wheel, thus implying an AFM ground state (Waldmann *et al.*, 1999). X-ray photoelectron and X-ray emission spectroscopy studies (Postnikov *et al.*, 2003a) allowed for probing of the electronic structure in the valence band and on the Fe site, albeit without resolution in spin. Whereas the magnetic measurements data are by now well established, the spatially resolved distribution of magnetization was not yet accessed prior to the present calculation. Specifically, we compare the results of electronic structure calculations by two different methods within the DFT, SIESTA and NRLMOL (see the discussion on the methods in Sec. 4). In both cases we used the generalized gradient approximation after Perdew, Burke and Ernzerhof (1996). We emphasize that the most important difference between two methods, in what regards the present study, is that SIESTA

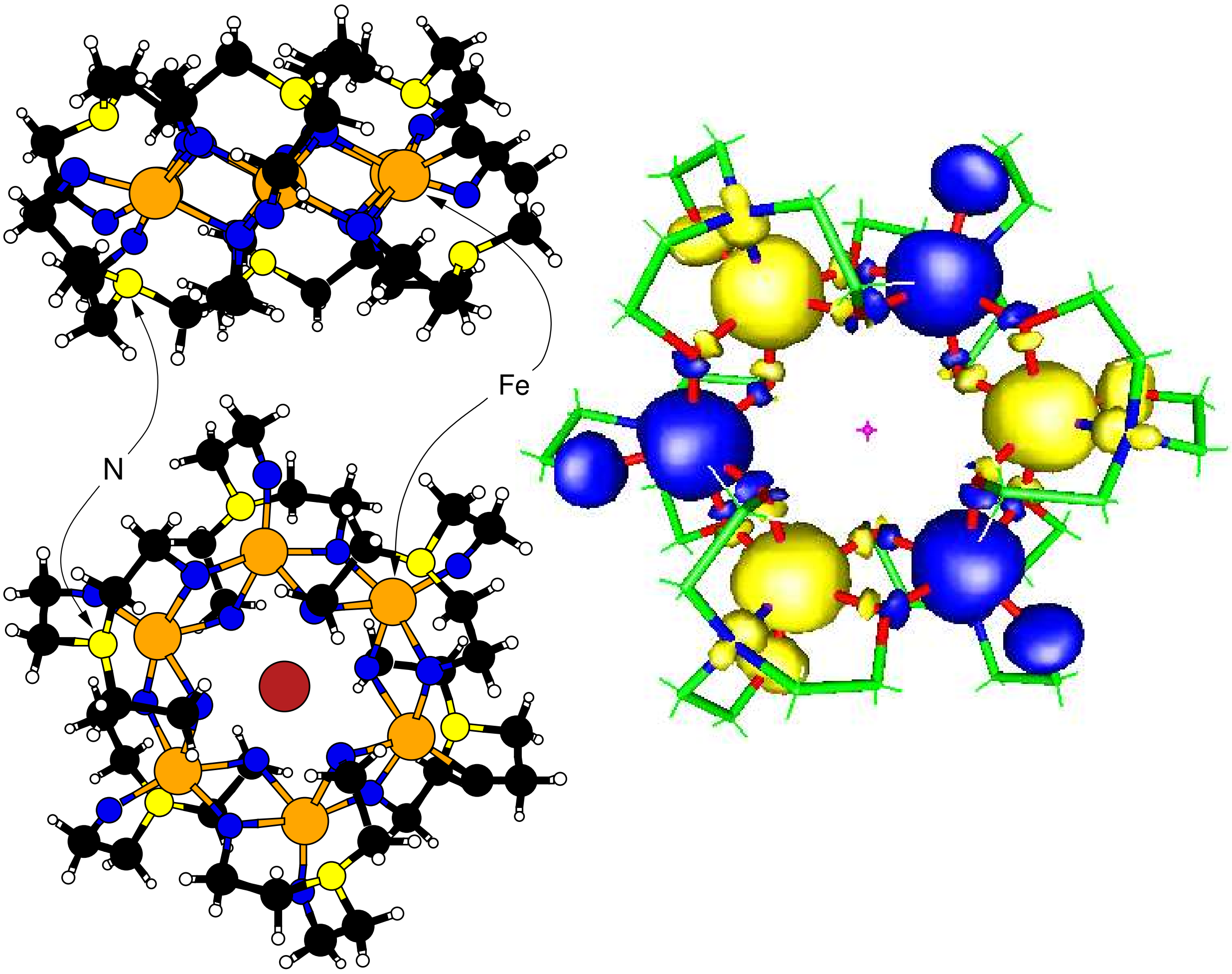


Figure 5: Structure and spin density distribution in “ferric wheel” molecules. Left panel: two views of the Li-centered molecule. The Li ion is in the middle of the ring; the distant Cl ion included in the simulation is not shown; the rest of (electrically neutral) solvent is neglected. Right panel: iso-surfaces correspond to $\pm 0.01 e/\text{Å}^3$, according to NRLMOL calculation (Postnikov *et al.*, 2003c). While most of the magnetic moment is localized at the Fe atoms, there is still some spin polarization on O and N.

uses norm-conserving pseudopotentials whereas NRLMOL implements an all-electron method. For an *ab initio* pseudopotential code such as SIESTA, benchmark calculations, based on the very accurate NRLMOL suite of codes, aid in accessing the accuracy of pseudo-potential based methods in some critical cases and/or for new systems.

We outline below the results obtained by SIESTA for the Li-centered molecule, and by NRLMOL – for the Na-centered one, as presented in more detail by Postnikov *et al.* (2003c). The NRLMOL treatment was restricted to the ground-state AFM configuration (alternating orientations of Fe magnetic moments over the ring); the SIESTA calculation addressed in addition different magnetic configurations, that allowed for the extraction of DFT-based exchange parameters.

Fig. 6 displays the partial densities of states (DOS) on Fe and its several neighbors in the AFM configuration, as calculated by both methods. The discrete levels of the energy spectra are weighted (with the charge density integrated over atom-centered spheres in NRLMOL, or

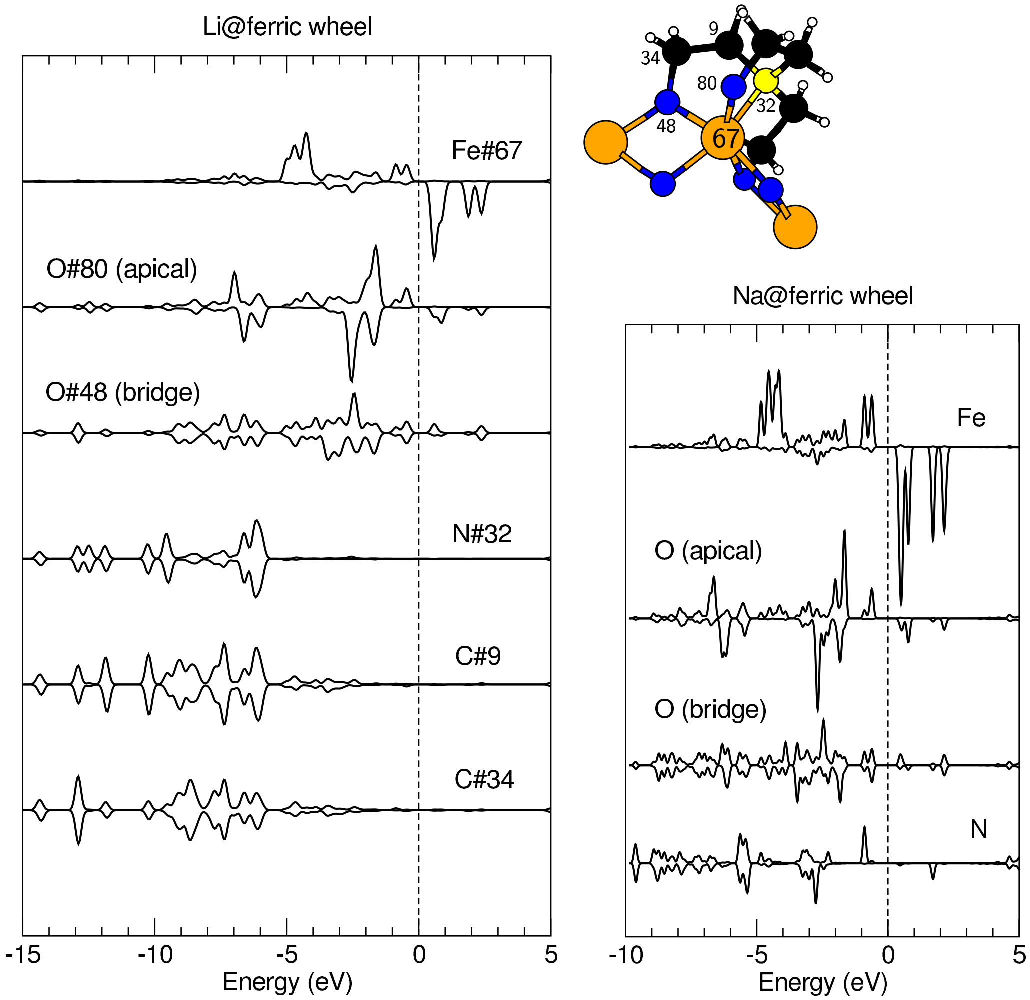


Figure 6: Atom- and spin-resolved partial densities of states as calculated for Li-centered molecule by Siesta (left panel) and for Na-centered molecule by NRLMOL (right panel). The DOS at the Fe site is scaled down by a factor of 2 relative to other constituents. The numbering of atoms which are neighbors to the Fe atom is shown in the inset. See text for details on the calculation.

according to Mulliken population analysis in Siesta), and broadened for presentational purposes with broadening parameter of 0.15 eV (Siesta) and 0.14 eV (NRLMOL). The local moments corresponding to integrating such partial DOS over occupied states are given in Table 2. Both calculations give a consistent description of state densities at Fe and O sites, even though this property is rather loosely defined (and its calculation differently implemented in Siesta and NRLMOL).

Notably, both methods find the local magnetic moments on Fe sites very close to 4 μ_B and *not* to 5 μ_B as is generally assumed, based on the above mentioned magnetization data. The maximal magnetization S=5/2 of the Fe atom corresponds to a Fe(III)-ion with in $3d^5_\uparrow d^0_\downarrow$ configuration. Our first-principles calculations suggest a somewhat different picture: the minority-spin DOS has a non-zero occupation due to the hybridization (chemical bonding) of Fe3d with O2p states. However, the magnetic polarization in the organic ligand which provides the octahedral coordination for the iron atoms, due to Fe is substantial, the most pronounced effect being on the apical oxygen atom (which is not participating in the bonding to the next Fe neighbor). Taken together with the (smaller) polarization of the bridging oxygen atoms and magnetization at the nitrogen site, the distributed magnetic moment *per* Fe atom yields 5 μ_B, recovering the agreement with the magnetization results.

A clear visualization of the above discussed delocalized (or, rather, distributed) magnetic moment associated with the Fe atom comes from the map of spin density, obtained from the NRLMOL calculation (Fig. 5, right panel). One should take into account that the volume enclosed by the iso-surfaces is not directly correlated to the total moment at the site. One sees moreover an absence of magnetization on carbon and hydrogen sites. The fact that the magnetization is noticeable and changes its sign when passing through bridge oxygen atoms emphasizes the failure of methods depending the spherical averaging of atom-centered potentials.

An important consequence is that the charge state of iron is not Fe(III) but more close to Fe(II), according to our (JK+AP) calculations. Moreover, the distributed magnetic moment behaves like a rigid one, in a sense that it can be inverted, following a spin flip on a Fe site. This is illustrated by the analysis of other magnetic configurations, done with SIESTA (Postnikov *et al.*, 2003a). The local DOS does not change considerably when switching from AFM to FM configuration – only the HOMO/LUMO gap becomes less pronounced, and a slight ferromagnetic shift between the two spin bands appears.

For the sake of improving both the stability of convergence with SIESTA and for pinning down a particular spin configuration (FM, or with one or more Fe magnetic moments inverted), we applied the FSM scheme (Schwarz and Mohn, 1984) in the calculation. Imposing an (integer) spin moment per molecule fixes the number of electrons in two spin channels and removes a possibility of spin flips, which are a major source of numerical instability, as there are many nearly degenerate states in the vicinity of the Fermi level in the molecule (and no symmetry constraints on these states in SIESTA). The FSM procedure would normally split the common chemical potential in two separate ones, for majority- and minority-spin channels, that corresponds to an effective external magnetic field and hence to additional (Zeeman) term in the total energy, in analogy with Eq. (4). Since molecular magnets possess a HOMO-LUMO gap, the latter correction must only be considered if such gaps in two spin channels do not overlap. Fig. 7 shows the total energy values and energy gaps for FSM values of 30 μ_B (FM case), 20 and 10 μ_B (one and two local moments inverted, correspondingly); 0 (alternate-spin AFM case). A linear change

Table 2: Local magnetic moments M at Fe and its neighbors. NRLMOL results correspond to spin density integrated over sphere of radius R centered at corresponding atom; SIESTA values are due to Mulliken population analysis.

Atom	R(a.u.)	$M(\mu_\mathrm{B})$, NRLMOL	$M(\mu_\mathrm{B})$, SIESTA
Fe	2.19	3.85	3.91
O (apical)	1.25	0.20	0.30
O (bridge)	1.25	±0.01	±0.02
N	1.32	0.07	0.09

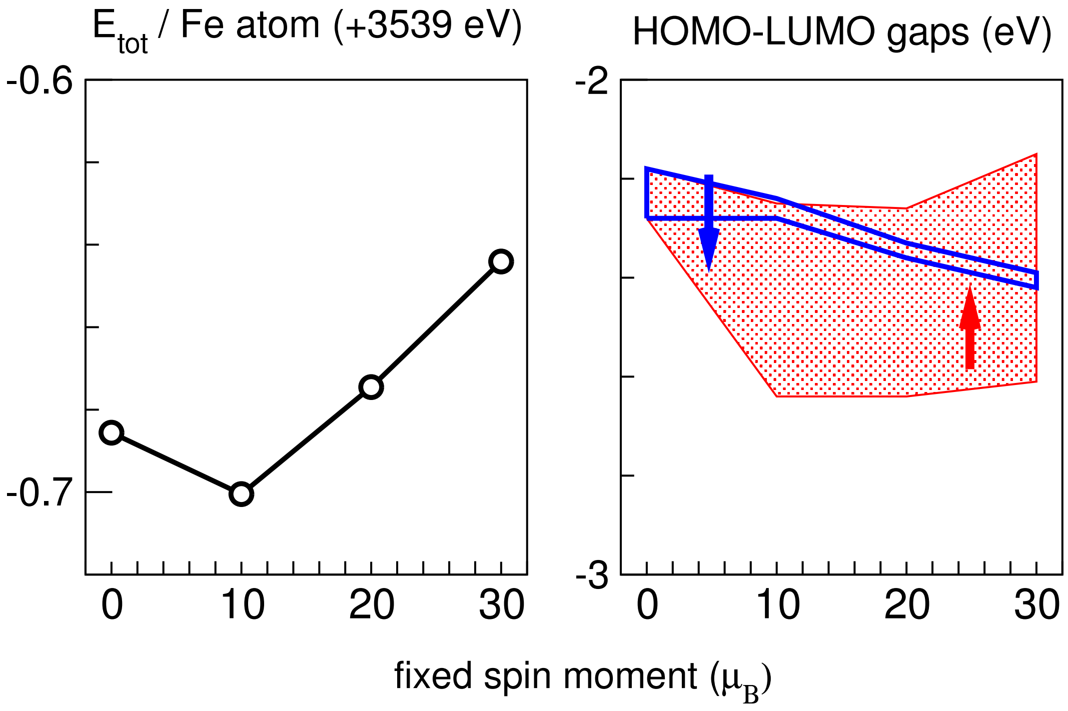


Figure 7: Total energy per Fe atom (left panel) and energy gap in two spin channels (right panel; shaded area – majority-spin, thick lines – minority-spin) from fixed spin moment calculations.

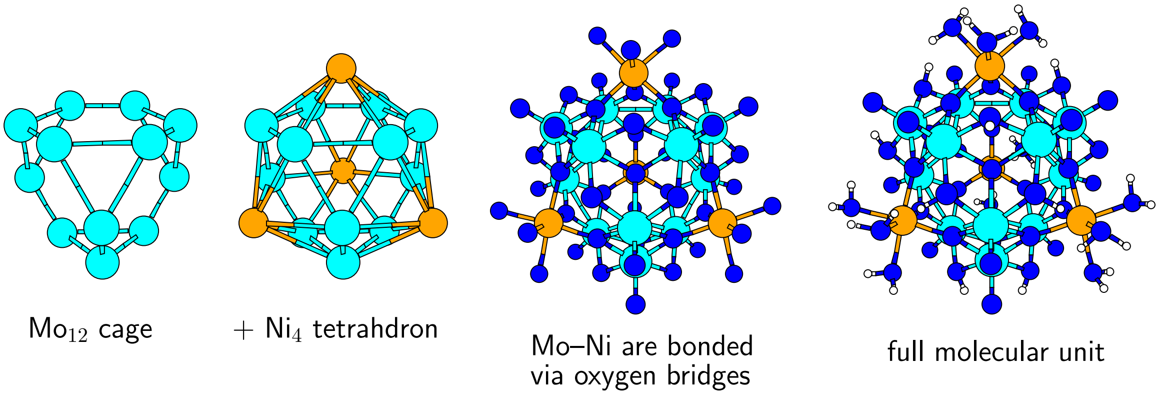
of the total energy while inverting one and then two local moments from the FM configuration is what would be expected from the Heisenberg model with “rigid” magnetic moments (in the sense that their S values do not depend on the total spin of the system), assuming moreover that only nearest-neighbors interactions between spins are important. An additional justification of the validity of the Heisenberg model comes from an observation that the magnitudes of local magnetic moments at Fe atoms always remain close (within several per cent) to 4 μ_{B}, and the partial DOS on Fe sites remains largely unaffected by the actual magnetic ordering. Similarly unaffected is a pattern of local magnetic moments at O and N neighbors of a particular Fe atom, always getting inverted as the latter experiences a spin flip. Keeping this in mind, and assuming Heisenberg-model spin Hamiltonian as in Section 1 with the S value of 5/2 (i.e., for the total spin which gets inverted), we arrive at the estimate for $-J$ of around 80 K (over both 30→20 and 20→10 μ_{B} flips). This is qualitatively correct (i.e. indicates a preference toward AFM coupling) and even of correct order of magnitude. However, two observations can be made here. First, the “true” AFM configuration (with half of magnetic moments inverted on the ring) does not follow the linear trend (see Fig. 7) and lies actually higher in energy than the configuration with two spins inverted. The origin of this is not yet clear to us at the moment. There are several possibilities, the zero-FSM configuration is, technically,the most difficult to converge, so some numerical instability can still play a role. On the other hand, a true (mixed) quantum-mechanical ground state of a system with six coupled S=5/2 spins may win over both our DFT solutions which correspond to selected values S_z=0 or S_z=5 of the total spin. Moreover, the necessity to include magnetic interactions beyond first neighbors, not yet considered at the moment, might further complicate the situation. The second observation concerns the magnitude of exchange parameter J and the fact that it is probably overestimated by a factor of ∼4 in our calculation.

The origin of this lies most probably in on-site correlations, which, if treated accurately beyond the standard schemes of the DFT, would primarily affect localized Fe3d states, shifting the bulk of occupied states downwards in energy, the bulk of unoccupied states upwards, expanding the energy gap, and – whatever scheme to use for estimating exchange parameters – substantially reducing their magnitude. This has been recently shown for another molecular magnet (Mn_{12}) by Boukhvalov *et al.* (2002) – see the discussion on Mn_{12} above and our analysis of a model binuclear system below.

Summarizing our analysis of the electronic structure of Li- and Na-centered “ferric wheels”, one can conclude that *local* magnetic moments on Fe sites seem to be 4 μ_B rather than 5 μ_B as is often assumed. This implies the valence state closer to Fe(II) than to Fe(III), with a substantial covalent part in the Fe–O bonding. The local spin of S=5/2 per iron site consistent with magnetization measurements is however recovered if one takes the magnetization of neighboring atoms into account. The ability to calculate Wannier functions in such systems may provide much more reliable estimates of projected moments than are currently offered by either Mulliken methods or methods based on moments within a sphere. It is the largest on the apical oxygen atom, followed by smaller moments on nitrogen and the bridging oxygen atoms. This picture is well confirmed by a spatial distribution of spin density.

With respect to its magnetic interactions, this system can be mapped reasonably well onto the Heisenberg model; hence we deal with *rigid* magnetic moments which are nevertheless *delocalized* – an interesting counter-example to a common belief that the Heisenberg model primarily applies to localized spins.

5.2 Ni_4



Mo_{12} cage

+ Ni_4 tetrahdron

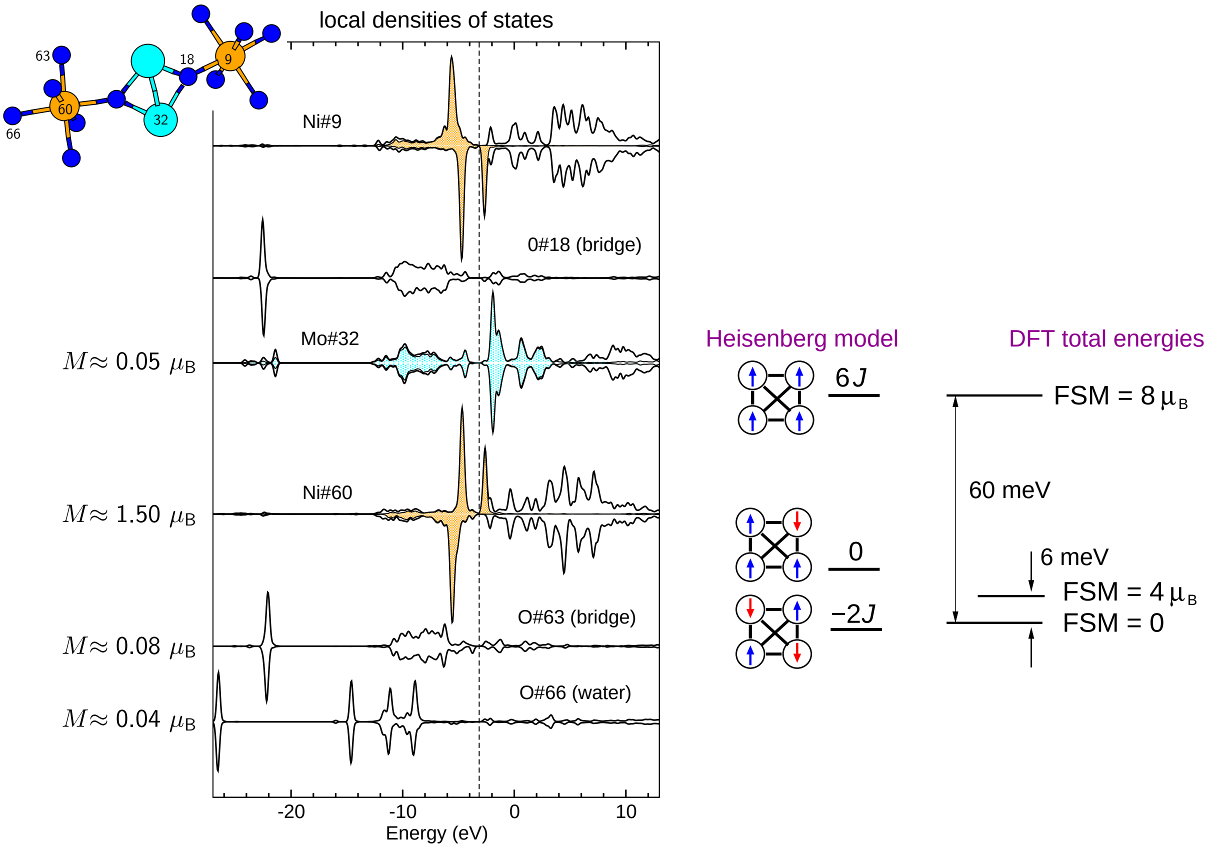
Mo–Ni are bonded via oxygen bridges

full molecular unit

Figure 8: Buildup of the “Ni_4” molecular unit.

“Ni_4” is a shorthand notation for a molecular crystal $[Mo_{12}O_{30}(\mu_2\text{–}OH)_{10}H_2\{Ni(H_2O)_3\}_4] \cdot 14\ H_2O$, synthetisized and characterized by Müller *et al.* (2000). This material crystallizes in a structure containing two formula units (shown in Fig. 8), related by the 180° rotation around an edge of the Ni_4 tetrahedron. The Ni–Ni distance is 6.6–6.7 Å, and magnetic interactions are mediated by a longer path than in the systems discussed above.

Magnetic properties are due to Ni^{II} ions in the $3d^8$ configuration (s=1); the ground state is an-



AFM configuration (broadening 0.2 eV).
Shaded areas indicate Ni$3d$ and Mo$4d$ contributions.

Figure 9: Left panel: local DOS of atoms at the Ni–Ni magnetic path. Right panel: a scheme of energy levels in different spin configurations of “Ni$_4$” according to the Heisenberg model and from first-principles calculations.

tiferromagnetic. An intriguing aspect of this compound is that the measured zero-field magnetic susceptibility can be very well mapped onto the Heisenberg model, whereas the measurements of magnetization cannot. The inclusion of different anisotropy terms in the Heisenberg model in order to improve the description of experiment had only limited success (Brüger, 2003). First-principles calculations have been performed using the Siesta method in order to access the electronic structure and estimate the magnitudes of magnetic interaction parameters.

Similarly as in the case of the “ferric-wheel” system discussed above, the FSM scheme was used for pinning down different spin configurations and comparing their total energies. The local DOS is practically indistinguishable for the cases of zero total moment (the AFM structure, which has indeed, in agreement with experiment, the lowest total energy) and configurations with local magnetic moments inverted at one or two Ni atoms (yielding, in the last case, the FM configuration). The local moment per atom in these cases agrees with the s=1 estimation derived from magnetization measurements. As was discussed above for other magnetic molecules, the magnetic moment is not fully localized on the Ni ion; small but non-negligible magnetization is induced on neighboring oxygen atoms, and even on more distant Mo atoms (Fig. 9, left panel). As the Ni–Ni interaction path is much longer than in other earlier discussed magnetic molecules (see inset in Fig. 9), the energy differences between configurations with FSM values

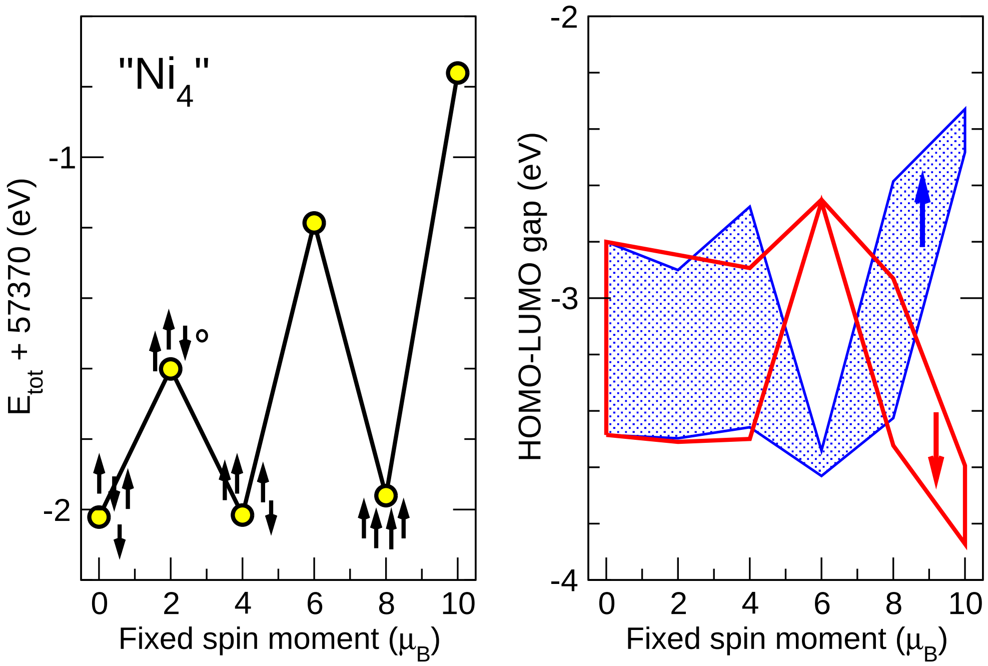


Figure 10: Total energy (left panel) and HOMO-LUMO gap (right panel) from FSM calculations of "Ni_4". See text for details.

of 0, 4 and 8 μ_{B} are small. These solutions are separated by other magnetic configurations which can be converged (2 and 6 μ_{B}) and correspond to a non-magnetic configuration of one Ni atom, with unchanged and differently coupled s=1 at three others (as schematically shown in Fig. 10, left panel). Energies of these intermediate configurations are substantially higher, and HOMO-LUMO gaps in two spin channels move apart, indicating the necessity of an external magnetic field (hence additional Zeeman energy) for stabilizing these artificial configurations. On the contrary, the three lowest-energy configurations have HOMO-LUMO gaps common for both spin directions (Fig. 10, right panel), therefore the mapping to the Heisenberg model can be done directly, without considering the Zeeman term.

An attempt of such mapping is schematically shown in the right panel of Fig. 9; obviously the sequence of energies of the configurations with one or two spins inverted (starting from the FM solution) is only in qualitative agreement with the Heisenberg model, but numerical energy differences do not allow for the evaluation of a unique value of J, in contrast to the case of "ferric wheel" discussed above. At best, one can make a rough estimate of the order of magnitude of $-J$, that yields 30 – 90 K.

This failure suggests that the magnetic interactions in "Ni_4" are strongly anisotropic. However, an adequate mapping of first-principles results onto models including the anisotropy would require the inclusion of spin-orbit interaction in the calculation, and this is not yet available in SIESTA. This feature is however included in NRLMOL and some of the progress along these lines is outlined below.

5.3 Magnetic anisotropy in single molecule magnets

As a modification of Eq. (4) which introduced the anisotropy in the simplest form, we distinguish in the following between axial and transverse anisotropy, with their corresponding parameters D and E. They enter the magnetic spin Hamiltonian (only second order terms) as follows:

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2), \tag{43}$$

The values of the axial anisotropy D are available from a number of experiments for different SMM, and for several SMM first-principle calculations have been carried out with the use of the NRLMOL code. These results are summarized in Table 3.

Table 3: Comparison of the calculated by NRLMOL and experimental magnetic anisotropy parameter D for the single molecule magnets. See theory references for computational details.

Molecule	S	D(K)	
		Theory	Experiment
$Mn_{12}O_{12}(O_2CH)_{16}(H_2O)_4$	10	−0.56[a]	−0.56[b]
$[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6Br_6]^{2+}$	10	−0.53[c]	−0.30[d]
$[Mn_{10}O_4$(2,2'-biphenoxide)$_4Br_{12}]^{4-}$	13	−0.06[e]	−0.05[f]
$Co_4(CH_2C_5H_4N)_4(CH_3OH)_4Acl_4$	6	−0.64[g]	−0.7 – −0.9[h]
$Fe_4(OCH_2)_6(C_4H_9ON)_6$	5	−0.56[i]	−0.57[j]
$Cr[N(Si(CH_3)_3)_2]_3$	3/2	−2.49[i]	−2.66[k]
$Mn_9O_{34}C_{32}N_3H_{35}$	17/2	−0.33	−0.32[l]
$Ni_4O_{16}C_{16}H_{40}$	4	−0.385	−0.40[l]
$Mn_4O_3Cl_4(O_2CCH_2CH_3)_3(NC_5H_5)_3$	9/2	−0.58[m]	−0.72[n]

[a]Pederson and Khanna (1999a,b), [b]Barra *et al.* (1997); Mertes *et al.* (2001), [c]Kortus *et al.* (2001b), [d]Dressel *et al.* (2003), [e]Kortus *et al.* (2002a), [f]Barra *et al.* (1999), [g]Baruah and Pederson (2002), [h]Murrie *et al.* (2003), [i]Kortus *et al.* (2002c), [j]Schromm *et al.* (2003), [k]Bradley *et al.* (1973), [l]Rajaraman and Wimpenny, [m]Park *et al.* (2003c), [n]Wernsdorfer *et al.* (2002).

In all the cases presented here the calculated spin ordering is in agreement with experiment. The calculated D parameters for Mn_{12}, Mn_{10}, Mn_9, the ferric star Fe_4 and Cr-amide molecular magnets are in excellent agreement with experimental values. The only remarkable discrepancy is found for Fe_8, a system which seems to pose complications for the DFT treatment. Apparently the DFT may be unable to predict the ground state density accurately enough due to important electronic correlations beyond the mean-field treatment or missing Madelung stabilization (absent in the isolated system).

The SMM listed in Table 3 are in general characterized by a high spin ground-state. However, a high spin state does not necessarily correlate with a high anisotropy barrier. The prefactor D is also very important. In order to increase the barrier one has to understand and control D, which will be the main goal of future research in this area. In all cases where the E parameter is not zero by symmetry it has been predicted with similar accuracy as D – see relevant references for details.

The results obtained make one confident in the predictive power of the formalism. It has been already mentioned that a microscopic understanding (based on the electronic structure of SMM) of the magnetic anisotropy parameters is crucial for the rational design of single molecule magnets.

In the following we will discuss some selected recent results of the not so well known single molecule magnets.

5.3.1 Co_4 magnet

A new Co-based ferromagnetic SMM with the complete chemical formula $Co_4(hmp)_4(CH_3OH)_4Cl_4$ (hmp^- is the deprotonated hydroxymethylpyridine), has achieved great interest due to the high anisotropy energy. A simulation by Baruah and Pederson (2002) resulted in the prediction of two new, energetically noncompetitive structural conformations with even higher anisotropy. Specifically, the magnetic anisotropy energy per Co atom was estimated from the experiment to be 25–50 K (Yang *et al.*, 2002). Although, newer experiments on a similar Co_4-cluster find significantly smaller total anisotropy energies of about 29 K (Murrie *et al.*, 2003), in better agreement with calculated values of 23, 160 and 50 K for the lowest energy and two higher energy phases found in the calculation. As already mentioned above, a large magnetic anisotropy is a prerequisite for potential applications of molecular magnets as "microdomains" for magnetic storage. An additional requirement, the existence of a net spin moment, is also satisfied here, with S=6 per molecular unit in the parallel (high spin) configuration, in all three isomers. Especially given that the earlier calculated results of Baruah *e*t al. compare more favorably with the more recent experimental results, a first-principle calculation might guide and stimulate practically relevant experimental research on this promising family of molecular magnets.

5.3.2 Fe_4-star

This material (of which several analogues with different central atom are known by now) realizes net spin moment in relatively compact and highly symmetric molecule due to AFM coupling of peripheric Fe atoms to the central one. The structure of the Fe_4 "ferric star" is shown in Fig. 11. All iron atoms are in the Fe^{3+} state, and the resulting ferrimagnetic arrangement has total $S = 5$. Similar to the other molecular magnets only states within an energy window of about 5 eV around the Fermi level contribute to the magnetic anisotropy. The symmetry of the cluster allows for a rhombohedral E contribution to the spin Hamiltonian. Using the experimental geometry (Schromm *et al.*, 2003) as a starting point for the calculation the theoretical value of $|E|$=0.064 K is in good agreement with the experimental one ($|E|$=0.056 K). [12] This agreement is relatively stable with respect to geometry changes. Total anisotropy barriers change normally only by a few K at most, although in some cases the agreement between theory and experiment becomes worse by optimizing the molecular geometry in the calculations. This can be understood because the geometry optimization is done for a single isolated molecule neglecting crystal packing effects

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[12] The sign of E depends on the definition of the axis.

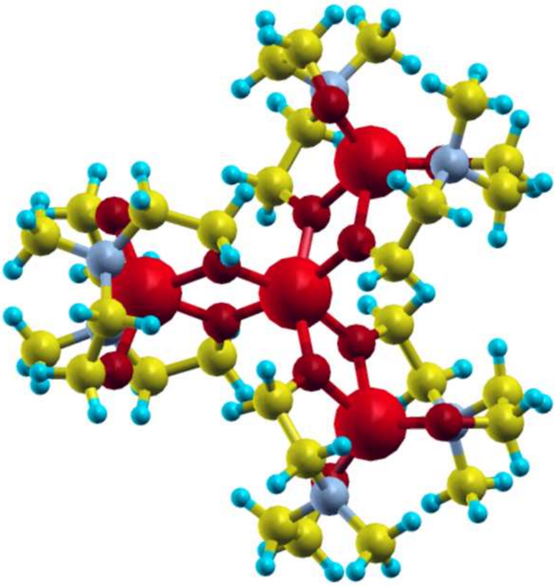

Figure 11: The molecular structure of the Fe_4-star. The Fe atoms are shown by large spheres.

and interactions in the molecular crystal which are important for the real molecular geometry.

5.3.3 Mn_{10} cluster

Ten Mn atoms form a tetrahedron-like structure with Mn atoms at the corners and at the middle of the tetrahedron edges, all bridged by oxygen ions (Barra *et al.*, 1999). Two of the Mn atoms are coupled antiferromagnetically to all the rest. The calculation by Kortus *et al.* (2002a) suggests an ionic picture that the first Mn has an Mn^{3+} ($S = 2$) state, whereas the other two are Mn^{2+} ($S = 5/2$). Due to the symmetry of the cluster, the two types of majority spin Mn atoms have a multiplicity of 4 whereas the minority spin Mn atom has a multiplicity of 2, resulting in the $S = 4\times2+4\times5/2-2\times5/2 = 13$ magnetic ground state. This magnetic core is further stabilized by organic rings which are also connected to the oxygen atoms. This molecular unit with the chemical formula $[Mn_{10}O_4$(2,2'-biphenoxide)$_4Br_{12}]^{4-}$ is charged and compensated by another molecular cluster containing a single manganese atom, $[(CH_3CH_2)_3NH]_2[Mn(CH_3CN)_4(H_2O)_2]$.

The calculations confirms the experimental suggestion that the magnetic anisotropy is only due to the functional unit containing 10 Mn atoms. The compensating cluster behaves paramagnetically with the Mn atom in a +2 charge state and spin $s = 5/2$. As shown by Kortus *et al.* (2002a), the single Mn-complex exhibits the easy-plane behavior with the energy well of only 0.1 K. The majority-spin gap in Mn_{10} is much smaller than the minority-spin one. Those matrix elements of Eq. (35) related to the occupied majority-spin states contribute in favor of an easy axis behavior whereas the matrix elements from the occupied minority-spin channel favor easy plane. These tendencies compete and cancel each other to a large extent. Only due to the larger contribution from the occupied majority-spin channel the complete Mn_{10} cluster ends up as an easy-axis system. Therefore, in spite of the fact that Mn_{10} possesses a high-spin state (S is larger than in Mn_{12}-ac), the anisotropy barrier in this system is small. Kortus *et al.* (2002a)

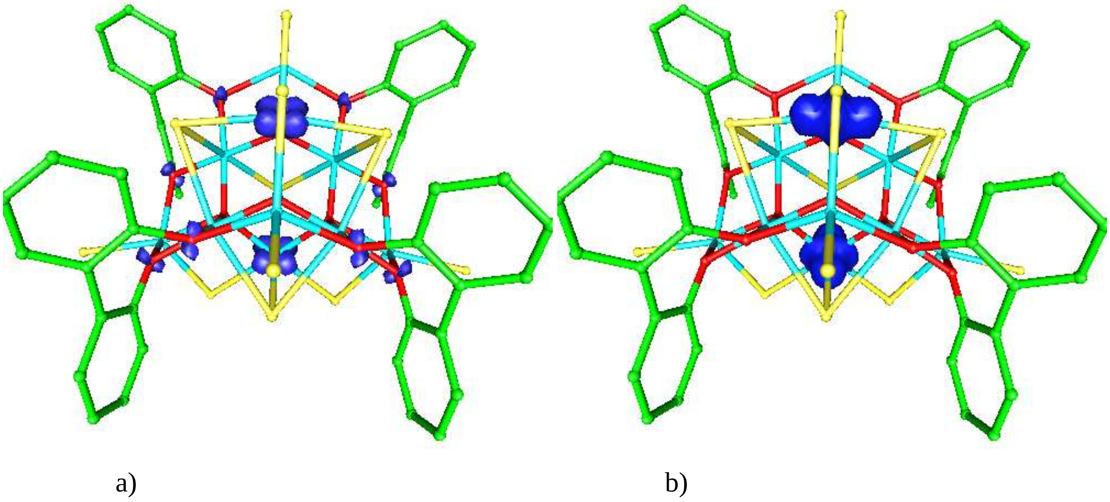
a) b)

Figure 12: Isosurface (dark blue) at 0.005 e/a_B^3 of the square of the wavefunctions (a: occupied majority state; b: unoccupied minority state) that contribute most to the matrix elements $M_{ij}^{\sigma\sigma'}$ of Eq. (35). Light blue: Mn, yellow: Br, red: O, green: C atoms. It is clearly visible that the matrix element connects majority and minority d-states at the same Mn atom.

found that the removal of subsets of the Br ions will change the magnetic anisotropy drastically due to large perturbations of the electronic structure. However, neutralizing the electric field due to Br ions by an external potential in the calculations changed the anisotropy barrier by less than 1 K. Therefore, one can conclude that the electric fields created by the Br ions do not have any significant effect on the magnetic properties of the molecule, in contrast to chemical interactions.

One of the advantages of the first-principles approach is the possibility to control in detail the interactions and states which are important for a certain physical property in order to gain a microscopic understanding. Eq. (35) shows that the barrier is related to matrix elements between occupied and unoccupied orbitals in the majority and minority spin channels. Besides the discrimination associated with spin pairing, we can analyze which electronic states mostly contribute to the matrix elements $M_{ij}^{\sigma\sigma'}$. In Fig. 12 we display plots of the square of the wavefunctions of the occupied majority state and the unoccupied minority state that contribute to the matrix element $M_{ij}^{\sigma\sigma'}$ with the largest absolute value.[13] It is clearly visible that the states of interest are d-states localized at the same Mn atom. In this case, the states are localized at the minority spin Mn atoms.

5.4 Some results of the V_{15} spin system

As already mentioned, the V_{15} system remains of great interest for studies on quantum coherence and relaxation phenomena, despite not having any sizeable magnetic anisotropy barrier (Chaboussant *et al.*, 2002; Chiorescu *et al.*, 2000; Gatteschi *et al.*, 1991; Kortus *et al.*, 2001a). The dynamics of the magnetization relaxation depends on the spin-phonon interaction at finite temperatures and an intrinsic phonon-bottleneck with a characteristic 'butterfly' hysteresis has

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[13] Please note, that the value of the magnetic anisotropy energy is not determined by a single dominant contribution, but results from the sum of many contributions with different signs.

been demonstrated by Chiorescu *et al.* (2000). Due to several very recent experimental studies on this system it became possible to check the quality of the electronic structure calculation. In a joint theoretical and experimental study by Boukhvalov *et al.* (2003) the system has been investigated using the LSDA+U band structure calculations [the same computational method as referred to above, for calculations by the same group on Mn_{12}-ac, Boukhvalov *et al.* (2002)] and measured X-ray photoelectron and fluorescence spectra. Comparing experimental data with the results of electronic structure calculations the authors conclude that the LMTO LSDA+U method provides a good description of the electronic structure of V_{15}.

Choi *et al.* (2003) report the reflectance and optical conductivity of solid V_{15} over a wide energy range. The band centered at 1.2 eV is assigned as a V dd transition, and other features at 3.7, 4.3, and 5.6 eV are attributed to Op-Vd charge transfer excitations. The comparison of the results to recent electronic structure calculations (Boukhvalov *et al.*, 2003; Kortus *et al.*, 2001a,b) show good agreement with all these calculations without clearly favoring any U value.

Chaboussant *et al.* (2002) report an Inelastic Neutron Scattering study of the fully deuterated molecular compound. They deliver direct confirmation that the essential physics at low temperature is determined by three weakly coupled spin-(1/2) on a triangle. Interestingly, the experiment allowed to determine the effective exchange coupling of 0.211 meV within the triangle and the gap between the two spin-(1/2) doublets of the ground state. This direct interaction had been predicted earlier by Kortus *et al.* (2001a) with an value of 0.55 meV.

The work by Kortus *et al.* (2001a) utilized an efficient coupled multilevel analysis which relied on fitting density-functional energies to mean-field Heisenberg or Ising energies in order to determine the exchange parameters. The approximate exchange parameters gleaned from the first N Ising configurations were used to find the next lowest energy Ising configuration and subsequently to improve the parameterization of the exchange parameters. The “self consistency” criterion in this approach was the check as to whether the predicted Ising levels remain unchanged under the addition of data from new Ising configurations. This mapping of DFT results on a classical Ising model allowed for the determination of the exchange parameters by considering only several spin configurations.

The data used to determine the exchange parameters from a least square fit to the mean-field solution of the Heisenberg Hamiltonian (Eq. 2) are displayed in Table 4. The fit is very good (with errors ranging from 0.1 to 1.55 meV) and leads to exchange parameters (in the notations of Fig. 4) of $J = 290.3$ meV, $J' = -22.7$ meV, J''=15.9 meV, $J1 = 13.8$ meV, $J2 = 23.4$ meV and $J3 = 0.55$ meV, where positive numbers correspond to AFM and negative to FM interactions. The *ferromagnetic* interaction J' is a surprising result and deserves further discussion since it is qualitatively different from earlier assumptions based on entirely AFM interactions (Chiorescu *et al.*, 2000; Gatteschi *et al.*, 1991). A FM coupling is possible without polarizing the oxygens through a fourth order process similar to super-exchange. In super-exchange, the intermediate state has the lowest d-orbital on the V atom doubly occupied with up and down electrons. However, electrons can also hop to higher energy d-orbitals. In this case both parallel and antiparallel spins are allowed without violating the Pauli exclusion principle, and consistently with the Hund’s first rule the parallel spin alignment is preferred. The superexchange (within the same d-orbital) completely excludes the electrons of the same spin electrons whereas the

Table 4: DFT energies (E in meV) of calculated Ising configurations, energies obtained from the fit, and $4\langle S_i^q S_j^q \rangle$ along each of the six bonds. Also included is the anisotropy shift δ for the $M_s = S$ state of each Ising configuration. A least square fit of this data leads to exchange parameters of J=290.3, J'=−22.7, J"=15.9, $J1$=13.8, $J2$=23.4 and $J3$=0.55 meV.

E	Fit	J	J'	J''	$J1$	$J2$	$J3$	Spin	Label	δ (K)
−78.37	−78.44	−6	2	−2	6	−6	−1	1/2	I	0.8
−73.39	−73.63	−6	2	−2	4	−4	−1	1/2	II	
−35.48	−35.08	−6	−2	2	4	−4	−1	1/2	III	
−34.89	−34.53	−6	−2	2	4	−4	3	3/2	IV	
0.00	−0.79	−6	−6	6	6	−6	3	3/2	V	1.5
8.38	8.28	−6	−6	6	2	−2	−1	1/2	VI	1.3
28.14	28.08	−6	−6	6	−6	6	3	3/2	VII	
126.32	126.14	−4	−4	6	4	−6	3	1/2	VIII	
129.17	128.88	−4	−4	2	6	−4	3	5/2	IX	
278.35	278.50	−2	−6	2	4	−4	3	3/2	X	
434.22	435.78	0	0	6	6	0	3	9/2	XI	1.6
760.75	760.76	6	6	6	−6	−6	3	9/2	XII	1.6
873.11	872.35	6	6	6	6	6	3	15/2	XIII	1.8

ferromagnetic process (different participating d-orbitals) merely favors FM alignment. Thus a FM coupling is obtained if the V-O hopping matrix elements into the higher d-orbital are significantly larger than the matrix elements for the hopping of O electrons into the lowest energy d-orbital. The occurrence of such interactions are possible in a low-symmetry system such as V_{15}. Even with this FM interaction, the spin Hamiltonian yields an S=1/2 ground state composed largely of Ising configurations similar to the one depicted in Fig. 4. This Ising configuration was predicted from the J's from the earlier fits to DFT energies and corresponds to the ground state DFT configuration (I).

Comparing the calculated susceptibility with experiment (Chiorescu *et al.*, 2000), one finds the that low-temperature behavior is not well reproduced and the doublet-quadruplet gap $\Delta \approx$ 10K is significantly larger than the experimental value of $\Delta \approx$ 3.7K, while the high-temperature behavior shows that calculated value of J is too large.

Both of these discrepancies can be explained almost entirely by a J that is too large within the density-functional-based treatment. The large value of J can be attributed to both exchange processes through the oxygens and to direct exchange between the V. If direct exchange is important, the value of J will be influenced greatly by the overlap between the V atoms. Electronic correlations included in form of LDA+U may help to improve the agreement with experiment, because the overlap between the d-orbitals of the vanadium atoms will be decreased by shifting the occupied d-orbitals down in energy by U. Similarly, self-interaction corrections (SIC) (Svane and Gunnarsson, 1988, 1990) will lower the magnitude of J because it will localize the V d-orbitals more, reducing the overlap of the wavefunctions.

Without including a direct exchange interaction between the vanadium atoms in the inner triangle ($J3 = 0$), reducing J to 70 meV and slightly reducing the difference between $J1$ and $J2$ yields the experimentally observed effective moment. Although, another set of only anti-ferromagnetic interactions (Gatteschi *et al.*, 1991) also fits the experimental results well. In fact any set of parameters with the correct values of J and Δ given by simple perturbation theory

$$\Delta = \frac{3}{4}\frac{(J2 - J1)^2(J'' - J')}{J^2} + \frac{3}{2}J3, \tag{44}$$

will fit the experimental effective moment well. The already mentioned problem of the parameter dependence on the assumed model arises here.

By including a possible direct interaction between the triangle vanadium atoms ($J3$) in the spin Hamiltonian the agreement with experiment can be achieved by dividing all J's by a constant factor of 2.9. Scaling of $J3$ down by a factor of 2.9 gives a value of 0.19 meV, in surprisingly good agreement with the corresponding value obtained from inelastic neutron scattering (Chaboussant *et al.*, 2002) of 0.221 meV. One possibility to decide between different models could be the measurement of the spin ordering and the spin-spin correlation functions by, e.g., neutron scattering.

5.5 A model Fe-binuclear system

Binuclear metal-organic systems form a large, and probably simplest, group among molecular magnets. Even if their magnetic characteristics like ordering temperature and bulk magnetization are not necessarily outstanding, they help to grasp important physics of $3d$–$3d$ magnetic interaction mediated by an organic ligand and thus offer a convenient model system. Moreover, an interesting effect of spin-crossover has been observed in some such systems, for instance in [Fe(bt)(NCS)$_2$]$_2$-bpym (bt= 2,2'-bithiazoline, bpym= 2,2'-bipyrimidine): a switch from LS-LS to LS-HS to HS-HS configuration (LS: low spin; HS: high spin) at the increase of temperature, where the intermediate LS-HS state gets stabilized near 170 K due to an interplay between intermolecular and intramolecular magnetic interactions (Ksenofontov *et al.*, 2001a,b; Létard *et al.*, 1999). One demonstrated the possibility of optical switching between different magnetic states and brought into discussion the prospects of their use as active elements in memory devices.

Our interest in binuclear systems is primarily that for model molecular magnets, to be treated with a method of recognized accuracy, and with the aim to look at the effect of intraatomic correlation effects ("Hubbard U"). Starting from the real structure of [Fe(bt)(NCS)$_2$]$_2$-bpym (see Fig. 13, left panel), we "streamlined" it somehow to fit it into a compact unit cell for an accurate calculation by a band structure method with periodic boundary conditions (Fig. 13, right panel). This transformation preserved the bipyrimidine part between two Fe centers, but "shortcut" the distant parts of ligands to make a connected structure. The calculation has been done with the FLEUR code (FLEUR homepage), a realization of full-potential augmented plane wave technique. One can see that, in contrast to "ferric wheels", the Fe atom is now octahedrally coordinated by nitrogen ions. A formal valence state in these compounds is routinely referred to as Fe(II). The HS and LS states were discussed to be represented by the $t_{2g}^4e_g^2$ and t_{2g}^6 configurations, correspondingly (Ksenofontov *et al.*, 2001b). Our calculation did not yet include

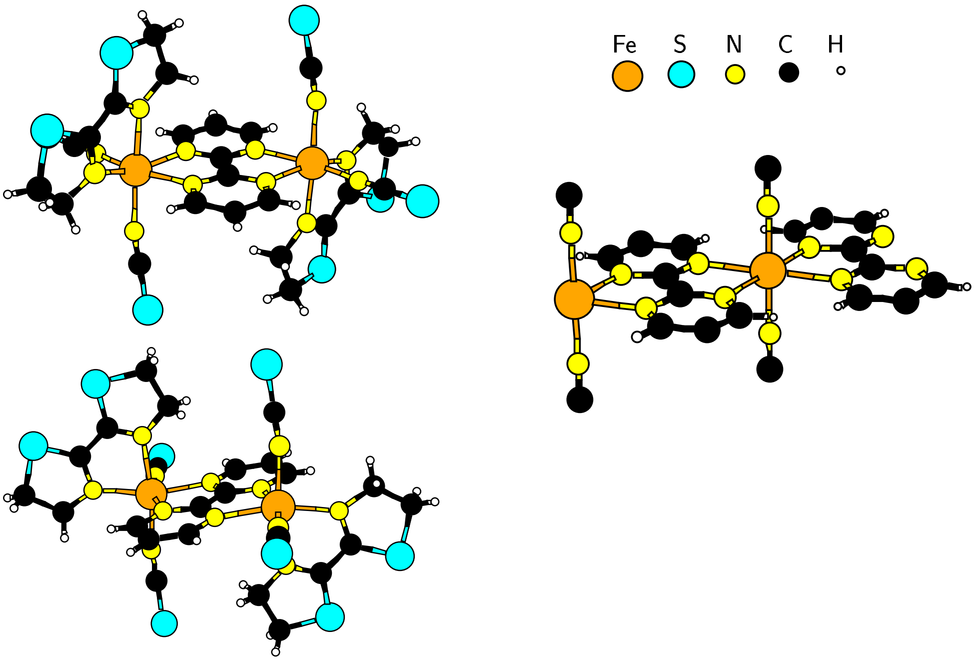

Figure 13: Two views of the $[Fe(bt)(NCS)_2]_2$-bpym molecule (left panel) and a simplified periodic Fe-binuclear system used in the FLEUR calculation (right panel).

the orbital transition of this type; we initialized only HS configurations and brought them into self-consistency in FM and AFM settings. The resulting partial DOS are shown in Fig. 14.

Certain similarities can be found with the Fe local DOS in "ferric wheels" – clear splitting into t_{2g}-like and e_g-like states in nearly octahedral ligand field, full occupation of majority-spin Fe3d states and one electron per Fe atom trapped in the Fe3d–N2p hybridized band of minority spin. The values of magnetic moments (total per Fe atom in the FM case, along with the local moment, integrated over the muffin-tin sphere) are listed in Table 5. The interatomic exchange parameters have been estimated from total energy differences between FM and AFM cases.

Table 5: Magnetic moments and interaction parameters as estimated for a model Fe-binuclear system (Fig. 13) from calculations by FLEUR with and without Hubbard U.

		M(Fe)	M/Fe	ΔE	J (S=5/2)
$U=0$	FM	3.62	4.10		
	AFM	3.61	–	102.5 meV	−190 K
$U=4$ eV	FM	3.93	4.94		
	AFM	3.92	–	76.8 meV	−143 K

Since the magnetic moment is largely localized at the Fe site, the inclusion of intraatomic correlations beyond the "conventional" DFT might be important. The exchange parameters J depend on the spatial overlap of the d-orbitals on different Fe-sites. It is well known that the d-orbitals within DFT are not localized enough compared to experiment, consequently the J values will be overestimated. There are two main reasons for this shortcoming. First, possible on-site

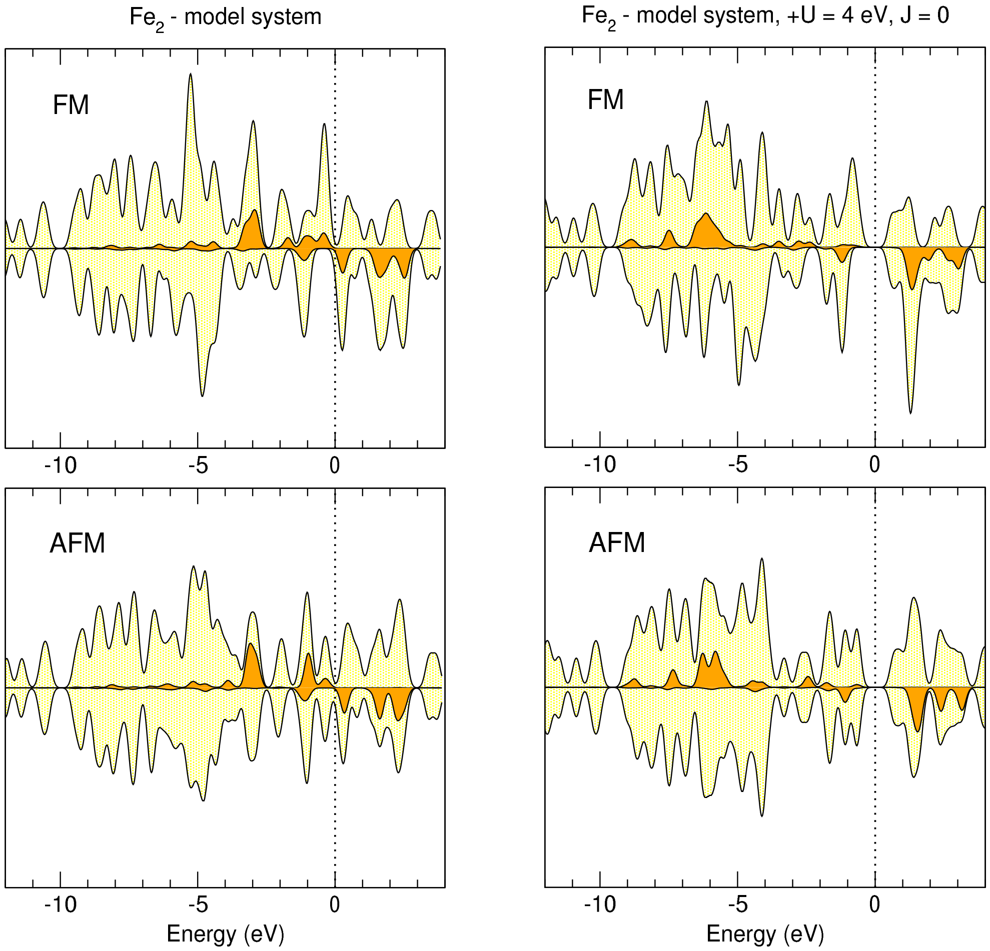

Figure 14: Densities of states in FM and AFM cases as calculated by FLEUR for the model Fe-binuclear system, in the DFT and in the LDA+U approach. Fe local DOS are shown as shaded areas.

correlations as known from atomic physics are underestimated in case of “conventional” DFT. Second, DFT is not free from spurious self-interactions due to the replacement of the point-like electrons by corresponding densities. Bringing in the atomic physics in the form of LDA+U (adding a local orbital dependent atomic Coulomb interaction parameter U to DFT (Anisimov *et al.*, 1997) or self-interaction corrections (SIC) (Svane and Gunnarsson, 1988, 1990) will improve the results by lowering the d-orbitals in energy and therefore localizing them stronger. SIC only affects occupied states, whereas LDA+U plunges the occupied d-states and shifts the unoccupied ones to higher energies. By increasing, on the average, the magnetic excitation energy across the spin majority-minority gap, both mechanisms help to effectively reduce the magnitude of J. To our knowledge, SIC have not yet been applied in calculations on molecular magnets (nor, are we aware of any practical implementation of SIC in a full-potential code, i.e., beyond the muffin-tin- or atomic sphere approximation. Baruah *et al.* are actively working toward a practical implementation of SIC within the NRLMOL suite of codes. The LDA+U scheme is implemented in the FLEUR code (as in many others). This *ansatz* has however a disadvantage of not being truly first-principles one: it remains on the user to single out certain orbitals as localized and to choose an appropriate value for the “Hubbard U” parameter. For

Fe-binuclear system we have chosen an empirically reasonable value U=4 eV; in principle, we were more interested in studying qualitative trends, as it deals with a model system anyway. One observes from Table 5 that the inclusion of intraatomic correlation enhances somehow the local magnetic moment at th Fe site, and to a much smaller extent – the total magnetic moment (in the FM configuration). Much more important, the J parameter is noticeably reduced due to correlation included. These observations agree with what was earlier reported by Boukhvalov *et al.* (2002) for the "Mn_{12}" system from the LDA+U calculation.

6 Conclusion

We attempted to give a broad overview of physical questions and technical problems one faces in modern first-principles simulations in the rapidly growing field of molecular magnets. Our own presented results largely correspond to work still in progress, and they might be far from providing an ultimative answer for particular systems. On the contrary, the results are likely to be refined and extended by subsequent studies. Our current results make us very confident in the predictive power of the presented methods. In order to explore the range of systems where the presented first-principles methods give reliable results, further studies on more systems are required. A large number of calculations are being performed by other groups on many other systems, which we might fail to name in this limited contribution. However, it is our hope that it may help the newcomers in the field to access the problems, the difficulties experienced and the possibilities offered by different methods and practical schemes of first-principles calculation. Many additional calculations are required to obtain a complete understanding of the idealized behaviors of molecular magnets and both new theory and new computational tools will be required to understand the nonidealities which will define the operating environments in applications of such systems.

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