SMR.2014

14th INTERNATIONAL WORKSHOP on COMPUTATIONAL PHYSICS AND MATERIALS SCIENCE: TOTAL ENERGY AND FORCE METHODS

8 - 10 January 2009

Miramare - Trieste, Italy

Co-sponsors:

- **International School for Advanced Studies (SISSA)**
- **INFM DEMOCRITOS National Simulation Center**
- **International Center for Materials Research (ICMR)**
- **Psi-k Network**
- **Centre Européen de Calcul Atomique et Moléculaire (CECAM)**

WEB page:
http://agenda.ictp.trieste.it/smr.php?2014

BOOK OF ABSTRACTS

ICTP

Scuola Internazionale Superiore di Studi Avanzati

· ma per seguir virtute e conoscenza ·

DEMOCRITOS

DEmocritos MOdeling Center for
Research in aTOmistic Simulation

INFM

icmr

Ψ_k

cecam

Centre Européen de Calcul
Atomique et Moléculaire

Organizing Committee:

R. Gebauer ICTP, Trieste, Italy
F. Mauri Université Pierre et Marie Curie, Paris, France
D. Vanderbilt Rutgers University, New Brunswick, USA

Scientific Committee:

A. Baldereschi EPF Lausanne, Switzerland
S. Baroni SISSA & DEMOCRITOS, Trieste, Italy
G. Galli University of California at Davis, USA
M. Gillan University College of London, UK
X. Gonze PCPM, Louvain-la-Neuve, Belgium
J. Ihm Seoul National University, Korea
E. Koch Forschungszentrum Jülich, Germany
S. Louie University of California at Berkeley, USA
N. Marzari MIT, Cambridge, USA
R. Needs University of Cambridge, UK
P. Ordejon ICMAB-CSIC, Barcelona, Spain
M. Parrinello ETHZ & CSCS, Zürich, Switzerland
L. Reining Ecole Polytechnique, Palaiseau, France
D. Vanderbilt Rutgers University, New Brunswick, USA

This book is also available in electronic format at the WEB site:
http://agenda.ictp.trieste.it/smr.php?2014

CONTENTS

The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

14th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

Cosponsor(s): the International School for Advanced Studies (SISSA), the INFM DEMOCRITOS National Simulation Center, the International Center for Materials Research (ICMR), the Psi-k Network, and the Centre Européen de Calcul Atomique et Moléculaire (CECAM)
Organizer(s): R. Gebauer, F. Mauri, D. Vanderbilt
Trieste - Italy, 08 - 10 January 2009

Venue: Leonardo da Vinci Building Main Lecture Hall

Preliminary Programme

REGISTRATION AND WELCOME (Room:Leonardo da Vinci Building Main Lecture Hall)

8 January 2009

08:00 - 08:50 (Room: Leonardo da Vinci Building, Lobby)
--- REGISTRATION and ADMINISTRATIVE FORMALITIES ---

08:50 - 09:00 **Organizers**
Welcoming Remarks

SESSION 1: Many-body Techniques for Real Materials (Room:Leonardo da Vinci Building Main Lecture Hall)

8 January 2009

09:00 - 09:35 **Geoffrey Stenuit** / *CNR-INFM Democritos, Trieste, Italy*
Bridging the size gap between density-functional and many-body perturbation theory

09:35 - 10:10 **Giulia Galli** / *UC Davis, USA*
Efficient evaluation of dielectric matrices for ab-initio calculations of excited state properties and correlation energies

10:10 - 10:45	**Gian-Marco Rignanese** / *Univ. Catholique de Louvain, Belgium* **Band offsets from many-body perturbation theory**
10:45 - 11:30	--- Coffee Break + Registration ---
11:30 - 12:05	**Huy-Viet Nguyen** / *Hanoi National University of Education, Viet Nam and SISSA, Trieste, Italy* **Efficient and accurate calculation of exact exchange and RPA correlation energies in ACFD theory**
12:05 - 12:40	**Lucia Reining** / *École Polytechnique, Palaiseau, France* **Correlation in electronic excitations**
12:40 - 14:40	--- Lunch ---

SESSION 2: Simulations of Structural Properties (Room:Leonardo da Vinci Building Main Lecture Hall)

8 January 2009

14:40 - 15:15	**Roberto Car** / *Princeton U., Princeton, USA* **Quantum protons in hydrogen bonded systems**
15:15 - 15:50	**Chris Pickard** / *St. Andrews, UK* **Ab-initio random structure searching: A window on structure space**
15:50 - 16:35	--- Coffee Break + Registration ---
16:35 - 17:10	**Ron Cohen** / *Carnegie Institution, USA* **Quantum Monte Carlo simulations of behavior at extreme conditions**
17:10 - 17:45	**Borje Johansson** / *Uppsala, Sweden* **TBC: Modeling materials at high pressure for earth sciences**

POSTER SESSION 1 (Room:Adriatico Guest House (Lower Level 1))

8 January 2009

17:45 - 18:30	--- Poster setup at Adriatico Guest House (Lower level 1) ---
18:30 - 21:00	**Poster session / free discussions** Informal buffet for all participants during the poster session

SESSION 3: 2008 ICTP Prize Ceremony (Room:Leonardo da Vinci Building Main Lecture Hall)

9 January 2009

08:50 - 09:35	**K.R. Sreenivasan** / *ICTP Director* **Welcoming Remarks and Presentation of the Award**
09:35 - 10:10	**Zhong Fang** / *Center for Quantum Simulation Sciences, CAS, Beijing, China* **LDA+Gutzwiller method for correlated electron systems**
10:10 - 10:45	**Abhishek Dhar** / *Raman Research Inst., Bangalore, India* **Green-Kubo formula for heat conduction in open systems**

10:45 - 11:30 --- Coffee Break ---

SESSION 4: Thermal and Electronic Transport (Room:Leonardo da Vinci Building Main Lecture Hall)

9 January 2009

11:30 - 12:05 **Davide Donadio** / *UC Davis, USA*
Thermal transport at the nanoscale

12:05 - 12:40 **Jeff Neaton** / *Molecular Foundry, LBNL, Berkeley, USA*
First-principles studies of single-molecule junction conductance: Links, length, and switching

12:40 - 14:40 --- Lunch ---

SESSION 5: Quantum Chemistry (Room:Leonardo da Vinci Building Main Lecture Hall)

9 January 2009

14:40 - 15:15 **Ali Alavi** / *Cambridge, UK*
Fermion Quantum Monte Carlo in slater determinant spaces: A game of life, death and annihilation

15:15 - 15:50 **Beate Paulus** / *Freie Universität Berlin, Germany*
Explicitly correlated ab initio methods for metals

15:50 - 16:35 --- Coffee Break ---

16:30 - 17:05 **Troy Van Voorhis** / *MIT, Cambridge, USA*
Constrained DFT for electron transfer and reaction barrier heights

17:10 - 17:45 **Jose Soler** / *Universidad Autónoma de Madrid, Spain*
Efficient first-principles van der Waals density functional forces

POSTER SESSION 2 (Room:Adriatico Guest House (Lower Level 1))

9 January 2009

17:45 - 18:30 --- Poster setup at Adriatico Guest House (Lower Level 1) ---

18:30 - 21:00 **Poster session / free discussions**
Informal buffet for all participants during the poster session

SESSION 6: Carbon Nanostructures (Room:Leonardo da Vinci Building Main Lecture Hall) (**Saturday**)

10 January 2009

08:50 - 09:00 **Organizers**
Introduction of Keynote Speaker

09:00 - 09:50 **Alex Zettl** / *UC Berkeley, USA*
Exploiting the Electronic, Thermal, and Mechanical Properties of Carbon and BN Nanostructures
Keynote talk in honor of STEVEN LOUIE's 60th Birthday

09:50 - 10:25	**Claudio Attaccalite** / *U. del Pais Vasco, San Sebastian, Spain* **Electron correlation in graphene: band structure and electron-phonon interaction from GW**
10:25 - 11:00	**Young-Woo Son** / *KIAS, Seoul, Korea* **Energy gaps in graphene superstructures**
11:00 - 11:45	--- Coffee Break ---

SESSION 7: Large-scale and Multi-scale Simulation (Room:Leonardo da Vinci Building Main Lecture Hall) (Saturday)

10 January 2009

11:45 - 12:20	**Karsten Reuter** / *FHI-MPG, Berlin, Germany* **Towards an error-controlled multi-scale catalysis modeling**
12:20 - 12:55	**Rosa di Felice** / *INFM-CNR, Modena, Italy* **Computational investigation of DNA derivatives for nano-electronics**
12:55 - 14:40	--- Lunch ---

SESSION 8: Functional Materials (Room:Leonardo da Vinci Building Main Lecture Hall) (Saturday)

10 January 2009

14:40 - 15:15	**Lilia Boeri** / *MPI-FKF, Stuttgart, Germany* **DFT studies of FeAs superconductors**
15:15 - 15:50	**Gianni Profeta** / *Università degli Studi dell'Aquila, Italy* **Hydrogen superconductivity and other superconductors**
15:50 - 16:35	--- Coffee Break ---
16:35 - 17:10	**Davide Ceresoli** / *MIT, Cambridge, USA* **Ab-initio pseudopotential calculations of the orbital magnetization**
17:10 - 17:45	**Ismaila Dabo** / *INRIA and Université Paris-Est, France* **First-principles electrochemistry**
17:45 - 17:55	**Concluding Remarks**

ABSTRACTS OF TALKS

(ordered according to programme)

Bridging the size gap between density-functional and many-body perturbation theory

G. Stenuit[1], *S. Baroni*[1,2], *P. Umari*[1]

1. CNR-INFM Democritos
2. SISSA

The calculation of quasi-particle spectra based on the GW approximation is extended to systems of hundreds of atoms, thus expanding the size range of current approaches by more than one order of magnitude. This is achieved through an optimal strategy, based on the use of Wannier-like orbitals, for evaluating the polarization propagator. Its potentials are demonstrated by addressing the quasi-particle spectra of model structures of vitreous materials, as well as of porphyrin-derived molecules.

Efficient evaluation of dielectric matrices for *ab-initio* calculations of excited state properties and correlation energies

Giulia Galli
University of California, Davis

We present an iterative approach to evaluate dielectric matrices [1], an discuss its use to carry out *ab-initio* calculations of excited state properties [2,3] and correlation energies [4]. In particular, we present a first principle technique to solve the Bethe-Salpeter equation (BSE) that builds on recent progress in time-dependent density functional perturbation theory [5], and does not require the explicit evaluation of excited single particle electronic states. We also discuss recent results on RPA correlation energies--obtained by solving the frequency dependent Sternheimer equation within linear response theory-- and we show that the use of an eigenmode representation of the dielectric matrix allows for a physical interpretation of several, different contributions to correlation energies.

[1] H.Wilson, F.Gygi and G.Galli, *Phys. Rev.* B **78**, 113303 (2008)
[2] D.Lu, F.Gygi and G.Galli. *Phys. Rev. Lett.* **100**, 147601(2008).
[3] D.Rocca, D.Lu and G.Galli (in preparation).
[4] D.Lu, H.Wilson and G.Galli (in preparation).
[5] D. Rocca, R. Gebauer, Y Saad, and S. Baroni, *J. Chem. Phys.* **128**,154105 (2008).

Band-offsets from Many-Body Perturbation Theory

G.-M. Rignanese[1,2,*]

1. European Theoretical Spectroscopy Facility (ETSF),
2. Unité Physico-Chimie et de Physique des Matériaux (PCPM),
Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgique.

Band offsets (BOs) are among the most important properties of a heterostructure. Their precise knowledge is extremely important to engineer electronic and optoelectronic devices. In this framework, density functional theory (DFT) calculations[1] reveal very powerful since no experimental input is required.
However, the DFT-BOs suffer from two important limitations: the well-known band-gap problem, and the use of an approximate exchange-correlation energy functional. Many-body perturbation-theory (MBPT) has thus been used to try to overcome these shortcomings[2,3] relying on various approximations (GW, plasmon pole model, potential lineup taken from DFT, ...).
Interestingly, for semiconductor interfaces, the MBPT corrections are almost the same on both sides of the interface, leading to BOs not very different from DFT. This explains why the latter is widely used to predict the BOs for a wide range of interfaces. When needed, the conduction BO is corrected using a scissor operator to match the band gap to its experimental value. However, when it comes to semiconductor-insulator or insulator-insulator interfaces, it appears that the DFT errors can be important even for the valence BO, emphasizing the need to go beyond DFT by including MBPT corrections.
In this presentation, I will examine the adequacy of the usual approximations used within MBPT to compute the BOs for the Si/SiO$_2$ interface. If time permits, I will also show some results for some other interfaces.

---

[*] Work done in collaboration with
R. Shaltaf, M. Grüning, and X. Gonze (Université catholique de Louvain, Belgium),
F. Giustino and A. Pasquarello (Ecole Polytechnique Fédérale de Lausanne, Switzerland).

[1] C.G. Van de Walle and R.M. Martin, Phys. Rev. B **34**, 5621 (1986).

[2] S. B. Zhang *et al.*, Solid State Commun. **66**, 585 (1988).

[3] X. Zhu and S. G. Louie, Phys. Rev. B **43**, 14142 (1991).

Efficient and accurate calculation of exact exchange and RPA correlation energies in ACFD theory

Huy-Viet Nguyen[1,2], *Stefano de Gironcoli*[1,3]

1. International School for Advanced Studies (ISAS-SISSA),
   via Beirut 2-4, I 34014, Trieste, Italy
2. Physics Faculty, Hanoi National University of Education,
   136 Xuan-Thuy, Cau-Giay, Hanoi, Vietnam
3. CNR-INFM DEMOCRITOS National Simulation Center,
   via Beirut 2-4, I 34014, Trieste, Italy

Recently there have been a renewed interest in the calculation of correlation energy for realistic systems in the Adiabatic Connection Fluctuation-Dissipation (ACFD) formalism, particularly within the Random Phase Approximation (RPA) for the exchange-correlation kernel. RPA correlation energy is an important ingredient in the so-called EXX/RPA(+) scheme, which has been shown to be a promising, though computationally very expensive, scheme to overcome the poor performance of standard LDA/GGA DFT in weakly bound systems [1,2,3,4]. In previous EXX/RPA+ calculations, based on plane-wave pseudopotential method [2,3,4], a very time-consuming step is the setup of the Kohn-Sham linear response function by performing summation over valence and conduction bands. In this talk, we will show that this step (and the calculation of the complete conduction state spectrum) is not needed and can be replaced by the iterative diagonalization of the RPA dielectric matrix via Density Functional Perturbation Theory (DFPT). We will also show that slow convergence of the exact-exchange energy with respect to Brillouin zone sampling can be alleviated by a careful treatment of the integrable divergence. We will demonstrate the efficency and accuracy of our implementation by studying a few bulk, molecular and atomic systems.

[1] F. Furche and T. Van Voorhis, J. Chem. Phys. **122**, 164106 (2005).
[2] M. Fuchs and X. Gonze, Phys. Rev. B **65**, 235109 (2002).
[3] P. García-González, J. J. Fernández, A. Marini and A. Rubio, J. Phys. Chem. A. **111**, 12458 (2007).
[4] J. Harl and G. Kresse, Phys. Rev. B **77**, 045136 (2008).

Correlation in electronic excitations

Matteo Gatti[1,2],*Federico Iori*[1,2], *Pina Romaniello*[1,2] *Lucia Reining*[1,2]

1. Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau, France
2. European Theoretical Spectroscopy Facility

To describe electronic correlations is one of the big challenges of condensed matter theory. In this talk, we will concentrate on features of correlation that can be detected in electronic spectra. We will discuss these features from the point of view of many-body perturbation theory, starting from the GW approximation [1]. We will focus on the role of the screened Coulomb interaction W; indeed it is simply the screening of the Coulomb interaction that makes the difference between Hartree-Fock and GW. Static screening gives rise to a renormalization of energies. Dynamical screening contains additional excitations that can be seen e.g. as satellites in photoemission spectra. We will discuss both aspects and their implications for theory and for the interpretation of experiments. Several systems will be used as illustration, in particular transition metal oxides.

[1] L. Hedin, Phys. Rev. **139**, A796 (1965)

Quantum protons in hydrogen bonded systems

Roberto Car[1]

1. Prinecton University

Quantum effects associated to protons play an important role in hydrogen bonded systems. In this talk I will discuss static equilibrium properties which can be calculated using Feynman's path integral formulation of statistical mechanics. I will focus, in particular, on the momentum distribution of the protons which is accessible in deep inelastic neutron scattering experiments. The momentum distribution is a property very sensitive to quantum character and provides a unique signature of tunneling events. Its accurate determination poses, however, challenges to both theory and experiment.

Ab initio Random Structure Searching: a window on structure space

Chris Pickard[1], *Richard Needs*[2]

1. School of Physics and Astronomy, University of St Andrews, St Andrews, KY16 9SS, UK
2. Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge, CB3 0HE, UK

Ab initio Random Structure Searching (AIRSS) is a strategy for predicting structures based on relaxation of randomly chosen starting configurations under the forces and stresses obtained from first principles electronic structure computations. By starting from random structures a wide coverage of the "structure space" is achieved, which allows for the possibility of finding radically new structures which have not been considered previously. The search strategy is remarkably straightforward and does not require the selection of highly-system-specific parameter values.[1]

The number of energy/enthalpy minima in the structure space is expected to increase exponentially with the number of degrees of freedom. We take no action to avoid local minima, and therefore our approach will certainly fail to locate the global minimum for large systems. However, it appears that our strategy works very well for systems with up to of order 10 atoms, which allows us to address many interesting problems. Further, larger systems can be handled through carefully chosen constraints, which tame the degrees of freedom.

I will demonstrate the power of AIRSS through applications to: silane,[1] hydrogen,[2] alane[3], nitrogen and ammonia.[4]

[1] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).

[2] C. J. Pickard and R. J. Needs, Nature Physics **3**, 473 (2007).

[3] C. J. Pickard and R. J. Needs, Phys. Rev. B **76**, 144114 (2007).

[4] C. J. Pickard and R. J. Needs, Nature Materials **7**, 775 (2008).

Quantum Monte Carlo Simulations of Behavior at Extreme Conditions

R.E. Cohen[1], *K. Driver*[2], *K. Esler*[1], *Z. Wu*[3], *B. Militzer*[3], *P.L. Rios*[4], *M. Towler*[4], *R. Needs*[4]

1. Geophysical Lab., Carnegie Institution
2. Ohio State University
3. University of California, Berkeley
4. University of Cambridge

We have studied silica and cubic BN under pressure using diffusion quantum Monte Carlo (DMC) with thermal free energies from phonons computed using density functional perturbation theory (DFPT) with the ABINIT code to obtain phase transition curves and thermal equations of state. We obtain excellent agreement with experiments for the metastable phase transition from quartz to stishovite. The local density approximation (LDA) incorrectly gives stishovite as the ground state. The generalized gradient approximation (GGA) correctly gives quartz as the ground state, but does worse than LDA for the equations of state. DMC, variational quantum Monte Carlo (VMC), and DFT all give good results for the ferroelastic transition of stishovite to the $CaCl_2$ structure, and LDA or the WC exchange correlation potentials give good results within a given silica phase. The ΔV and ΔH from the $CaCl_2$ structure to α-PbO_2 is small, giving uncertainly in the theoretical transition pressure. We have developed a fundamental high-temperature and high-pressure scale using cubic BN. The anharmonic Raman frequency was determined by solving the anharmonic Schrodinger equation for the vibrational well determined using QMC with the frozen phonon method. We obtain the static EOS for cBN up to 1 TPa. We include a novel correction based on all-electron LAPW wave functions to eliminate pseudopotential error. We also show that QMC yields more accurate Raman frequencies than standard DFT functionals.

Modeling materials at high pressure for earth science

Börje Johansson

Department of Physics and Materials Science
Uppsala University, Sweden

LDA+Gutzwiller Method for Correlated Electron Systems

Zhong Fang, and Xi Dai

Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

We will introduce our newly developed *ab initio* LDA+Gutzwiller method, in which the Gutzwiller variational approach is naturally incorporated with the density functional theory (DFT) through the "Gutzwiller density functional theory (GDFT)" (which is a generalization of original Kohn-Sham formalism). This method can be used for ground state determination of electron systems ranging from weakly correlated metal to strongly correlated insulators with long-range ordering. We will show that its quality for ground state is as high as that by dynamic mean field theory (DMFT), and yet it is computationally much cheaper. In addition, the method is fully variational, the charge-density self-consistency can be naturally achieved, and the quantities, such as total energy, linear response, can be accurately obtained similar to LDA-type calculations. Applications on several typical systems will be presented, and the characteristic aspects of this new method will be demonstrated. Finally, by applying this method to FeAs-based compounds, we will show that some of the difficult issues, such as the Fe-As bond length and the magnetic moment of the SDW state, can be solved.

References:
[1] X. Y. Deng, X. Dai, Z. Fang, EPL 83, 37008 (2008).
[2] G. T. Wang, X. Dai, Z. Fang, PRL 101, 066403 (2008).

Green-Kubo formula for heat conduction in open systems

Anupam Kundu[1], *Abhishek Dhar*[1], *Onuttom Narayan*[2]

1. Raman Research Institute, Bangalore 560080, India.
2. Department of Physics, University of California, Santa Cruz, CA 95064, US.

I will talk about an an exact Green-Kubo type linear response result for the heat current in an open system. The result is derived for classical Hamiltonian systems coupled to heat baths. Both lattice models and fluid systems are studied and several commonly used implementations of heat baths, stochastic as well as deterministic, are considered. The differences with the usual Green-Kubo formula and some possible applications of the present formula will be pointed out.

Thermal transport at the nanoscale

Davide Donadio[1], *Giulia Galli*[1]

1. Department of Chemistry, University of California, Davis

Silicon is one of the best known materials of our age, cheap and readily available, being the basic constituent of semiconductor electronics. It would therefore be highly desirable to broaden its utilization for, e.g. renewable energy applications. Recently, it has been proposed that Silicon may be engineered at the nanoscale to be an efficient thermoelectric material for use in solid state devices. Although a rather inefficient thermoelectric in its bulk form, at the nanoscale Si may become a poor heat conductor, while retaining good electronic conduction properties, and thus exhibit high efficiency in converting heat into electric current. However the fundamental reasons for the reported low heat conduction in Si nanowires (NW) are not yet understood, and different interpretations has so far appeared in the literature. This motivates an extensive study of thermal transport in quasi-one dimensional systems, from Carbon nanotubes to silicon wires. Here we focus on the atomistic simulations of heat conduction in Si NW of 1 to 3 nm diameter. Our results show that, depending on their surface structure, these wires may exhibit values of the thermal conductivity varying by two orders of magnitude, and as high as those of bulk Si. This clearly indicates that the increased surface to bulk ratio at the nanoscale may be only partially responsible for the decreased thermal conductivity observed experimentally. We also find that diffusive, yet extended, vibrational modes present in the case of wires with amorphous surfaces, are responsible for a dramatic decrease of a factor of 100 in the conductivity of purely crystalline NWs. Our findings suggest ways of engineering wires with even lower thermal conductivity, by increasing surface disorder, in particular by alloying Si with, e.g. Ge at the crystalline-amorphous interface.

First-Principles Studies of Single-Molecule Junction Conductance: Links, Length, and Switching

Jeffrey B. Neaton

Molecular Foundry, Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA

A fundamental challenge in nanoscience is to predict and understand the charge transport properties of individual molecules. Recent measurements [1] of the electrical conductance of single-molecule junctions − small aromatics linked to macroscopic gold electrodes by amine and pyridine endgroups − provide a unique opportunity to benchmark standard first-principles methods while quantitatively exploring fundamental mechanisms of molecular-scale charge transport. Here I will describe work using a scattering-state technique [2] based on density functional theory (DFT) to understand reported conductance measurements of single-molecule junctions. Using a physically motivated approximate self-energy correction based on GW calculations of metal-molecule interfaces [3,4], we explore quantitatively how junction geometry, link chemistry, and molecular length can affect transport properties and lead to novel behavior, such as reversible conductance switching [5]. The importance of many-electron corrections beyond DFT for accurately computing electronic level alignment and molecular junction conductance − and understanding experiments − is emphasized in light of our results. This work was supported in part by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

[1] L. Venkataraman et al, Nano Lett. **6**, 458 (2006); Nature **442**, 904 (2006)
[2] H. J. Choi et al, Phys. Rev. B **76**, 155420 (2007)
[3] J. B. Neaton et al, Phys. Rev. Lett. **97**, 216405 (2006)
[4] S. Y. Quek et al, Nano Lett. **7**, 3477 (2007)
[5] S. Y. Quek et al, submitted (2008)

Fermion Quantum Monte Carlo in Slater Determinant spaces: a game of life, death and annihilation

Ali Alavi[1] *and George Booth*[1]

1. Department of Chemistry, University of Cambridge, CB2 1EW, UK

A Quantum Monte Carlo method based on sampling Slater determinants will be presented. In particular, we have developed a population dynamics algorithm which controls an evolving population of positive and negative walkers (or, more appropriately, they can be called "spawners"). These spawners live, procreate, annihilate and die on Slater determinants, according a simple set of rules which resembles a type of "game of life". The rates for the procreation processes are determined by the off-diagonal matrix elements of the many-body Hamiltonian under study, whilst the death processes are determined by the diagonal matrix elements together with a self-consistently generated chemical potential, which yields the correlation energy. No fixed-node approximation is applied. The long time evolution of this population is shown to be able to sample the ground-state of the underlying many-body Hamiltonian. We will present applications of this algorithm to real systems, and comparison is made where exact benchmarks are available.

Explicitly correlated ab initio methods for metals

Beate Paulus

Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

Ab initio electron correlation calculations based on quantum-chemical methods are successfully applied to metallic systems. To deal with the two distinct problems that occur in metals, the difficulty of localization of the orbitals and the generation of clusters with neutral atoms in the center, we suggest an embedding scheme which has itself no metallic character but can mimic the metal in the internal region, where the atoms are correlated. The long range non-additive contributions of metalicity and correlation are treated with the method of increments. The approach has been applied to the group 2 and 12 metals (Be, Mg, Zn, Cd, and Hg). The obtained ground-state properties are shown to agree well with the experimental values. Moreover, taking into account the advantage of the method of increments to analyse the individual contributions to correlation energy it is possible to clarify some aspects of the structural features of the group 12 metals.

Constrained DFT for electron transfer and reaction barrier heights

Troy Van Voorhis[1]

1. MIT Department of Chemistry

Electron transfer reactions are the centerpiece of artificial photosynthetic complexes, organic LEDs and essentially all of redox chemistry. This talk will highlight ongoing work being carried out in our group aimed at developing methods that can accurately simulate the reaction dynamics in these types of systems. Specifically, this talk will focus on the electronic structure problem inherent in describing electron transfer: How can we treat charge transfer states on the same footing with the electronic ground state? How do we make connections between a phenomenological picture like Marcus theory and a more rigorous approach like DFT? How do we describe bond formation (in particular proton transfer) that is often intimately connected with the process of electron transfer? Time permitting, we will mention some applications of these methods to organic light emission, photoinduced dynamics and/or redox catalysis.

Efficient first-principles van der Waals density functional forces

Guillermo Román and José M. Soler,

Dep. Física de la Materia Condensada, C-III.
Universidad Autnoma de Madrid, E-28049 Madrid, Spain

The LDA and GGA functionals have established themselves as the non empirical methods of choice for large system calculations. However, their inability to describe nonlocal dispersion forces limits severly their application to many such systems of large interest, like molecular solids and liquids, physisorbed molecules on surfaces, and interactions between biological molecules. Several schemes have been proposed to overcome this limitation by adding ad-hoc atom-atom or atom-electron potentials, fitted to experiment or to quantum-chemistry calculations. But dispersion is really an electron-electron correlation effect, that must be described by an appropriate electron density functional, such as that proposed by Dion et al (PRL 92, 246401 (2004)). It is a true universal and general-purpose DFT functional, capable of describing semiquantitatively the week dispersion interactions, without compromising the accuracy of the best GGA functionals for stronger ionic, covalent and metallic bonds. Its direct evaluation for large molecular systems is very expensive, however, because it requires a double integral in real space, with the kernel integrand depending on the electron density at both points. We present a new implementation that avoids this N^2 scaling by applying Fourier convolution techniques to an accurately interpolated kernel. The resulting method scales as $N \log N$ and it allows to perform vdW-DFT simulations of essentially any system that can be simulated with GGA. We have applied the method to calculate binding energies and barriers of relative translation-rotation in double-wall carbon nanotubes.

Exploiting the Electronic, Thermal, and Mechanical Properties of Carbon and BN Nanostructures

A. Zettl[1]

1. Department of Physics, University of California at Berkeley, and Materials Sciences Division Lawrence Berkeley National Laboratory, Berkeley, USA

Planer and tubular forms of carbon and boron nitride exhibit unusual transport and mechanical properties. It is now possible to construct nanoscale devices that perform (often quite efficiently) specific functions, including electronic rectification, bandpass filtering, amplification, and mechanical actuation or transduction. The challenge is creating a higher-order (and still nanoscale) system from such components, i.e. full integration. I will discuss novel approaches to the integration issues. Nanomaterials can also be exploited for facilitating ultra-high sensitivity and ultra-high resolution electron microscopy, and I will discuss recent advances in this area. Theory can, and has been, critical to many of the experimental advances.

Electron correlation in graphene: band structure and electron-phonon interaction from GW

C. Attaccalite[1], *M. Lazzeri*[2] *L. Wirtz*[3] *A. Rubio*[1] *F. Mauri*[2]

1. ETSF European Theoretical Spectroscopy Facility and Universidad del Pais Vasco, San Sebastian, Spain
2. IMPMC, Universite Paris 6 et 7, CNRS, IPGP, 140 rue de Lourmel, 75015 Paris, France
3. Institute for Electronics, Microelectronics, and Nanotechnology, CNRS, 59652 Villeneuve dAscq, France

We studied the effect of electron-electron correlation on the full three dimensional dispersion of the pi-bands, Fermi velocities and effective masses of graphite/graphene within GW approximation. The results are then compared with recent experiments obtained by angle resolved photo-emission spectroscopy. The band structure obtained by density-functional theory (in LDA approximation) strongly underestimates the slope of the bands. Including GW corrections, however, yields remarkable agreement in the vicinity of the Fermi level. Successively we studied the effect of electronic correlation on the electron-phonon coupling (EPC) using different approximations, ranging from Hartree-Fock to GW. We found that GW renormalize the EPC at the A_1' $\mathbf{K}$ mode by almost 80% with respect to density functional theory in LDA or GGA approximation. The obtained phonon slope of the A_1' $\mathbf{K}$ is almost two time larger than the GGA or LDA one, in agreement with phonon dispersions from inelastic x-ray scattering and Raman spectroscopy.

Energy gaps in graphene superstructures

Young-Woo Son

Korea Institute for Advanced Study, Seoul 130-722, Korea

In this talk, based on first-principles calculations, I will discuss various ways to induce energy gaps in graphene. First, for graphene nanoribbons which have homogeneous edges on both sides, it is shown that there are energy gaps with special characteristics depending on their edge shapes and widths [1,2]. The gaps in graphene nanoribbons are also shown to be sufficient for room temperature applications [3,4]. Second, for epitaxial graphene grown on SiC(0001) surface, there is an energy gap at the Dirac point due to the sublattice symmetry broken interaction between reconstructed SiC surface and epitaxial graphene [5].

[1] Y.-W. Son, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006).
[2] Y.-W. Son, M. L. Cohen, S. G. Louie, Nature **444**, 347 (2006).
[3] L. Yang, C.-H. Park, Y.-W. Son, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. **99**, 186801 (2007).
[4] U. Choi, Y.-W. Son, in preparation (2008).
[5] S. Kim, J. Ihm, H. J. Choi, Y.-W. Son, Phys. Rev. Lett. **100**, 176802 (2008).

Towards an error-controlled multi-scale catalysis modeling

Karsten Reuter[1]

1. Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin (Germany)

Computational modeling is becoming a key contributor in modern materials science, pushing novel hierarchical approaches that integrate various levels of theory into one multi-scale simulation and span disparate regions in length and time. Critical to assigning the desired predictive quality to such simulations are robust links between the theories with error-control across the scales. At each scale, simulations have approximations that introduce uncertainty, and bridging from one scale to another gives rise to additional uncertainty. Only a stringent control of how these multiple sources of uncertainty affect the final multi-scale results allows to propagate an initial base accuracy up the increasing length and time scales. Obviously, if this base accuracy is not of predictive quality, there is little hope that accurate predictions can be made at any level of modeling that follows.

Using examples from heterogeneous catalysis, I will sketch our efforts towards such an error-controlled multi-scale modeling using density-functional theory and kinetic Monte Carlo to treat the electronic and statistical levels, respectively. I will illustrate the use of sensitivity analyses to establish robust links between the theories and the use of a local exchange-correlation (xc) approach to establish an accurate energetic basis even for binding interactions that challenge present-day DFT xc functionals.

Computational investigation of DNA-derivatives for nano-electronics

Rosa Di Felice

National Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR, Modena, Italy

The unique self-assembling and recognition properties of DNA make it appealing for the realization of DNA-based nano-electronics. However, contoversial experimental data reveal a complex situation. To improve the significance of the data, two concurrent options are currently followed: (1) improve the measurement setup; (2) look for alternative DNA-based candidates that possibly host faster electron transfer. The latter can be based on alterations of either the nucleobase chemistry or the helical motif. I will illustrate how ab initio electronic structure calculations and molecular dynamics simulations can elucidate the electronic and structural properties of native and modified DNA structures. In particular, I will show results and discussion about density-funtional-theory (DFT) and molecular dynamics studies of G4-DNA [1], time-dependent DFT studies of DNA and xDNA [2], DFT studies of M-DNA [3] and natural DNA [4].

[1] (a) A. Calzolari, R. Di Felice, E. Molinari, A. Garbesi, *Appl. Phys. Lett.* **80**, 3331 (2002). (b) H. Cohen, T. Sapir, N. Borovok, T. Molotsky, R. Di Felice, A. B. Kotlyar, D. Porath, *Nano Letters* **7**, 981 (2007). (c) M. Cavallari, A. Calzolari, A. Garbesi, R. Di Felice, *J. Phys. Chem. B* **110**, 26337 (2006).

[2] (a) D. Varsano, A. Garbesi, R. Di Felice, *J. Phys. Chem. B* **111**, 14012 (2007). (b) D. Varsano, R. Di Felice, M. A. L. Marques, A. Rubio, *J. Phys. Chem. B* **110**, 7129 (2006).

[3] G. Brancolini, A. Garbesi, Rosa Di Felice, *J. Phys. Chem. B* **112**, 14281 (2008).

[4] E. Shapir, A. Calzolari, C. Cavazzoni, D. Ryndyk, G. Cuniberti, A. B. Kotlyar R. Di Felice, D. Porath, *Nature Materials* **7**, 68 (2008).

Coworkers at S3: A. Calzolari, D. Varsano, M. Cavallari, G. Brancolini, A. Garbesi, E. Molinari. External collaborators: D. Porath (Hebrew University of Jerusalem, Israel; A.B. Kotlyar (Tel Aviv University, Israel); A. Rubio (Universidad del Pais Vasco, San Sebastian, Spain); J.M. Soler (Universidad Autonoma de Madrid, Spain).

DFT studies of FeAs Superconductors

Lilia Boeri[1],
O.V. Dolgov [1], *A.A. Golubov*[2], *O.K. Andersen*[1]

1. MPI-FKF, Heisenbergstrasse 1, D70569 Stuttgart, Germany

2. Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

Superconductivity in the F-doped iron pnictides was discovered early in 2008. Within a few months, T_c was increased from 26 K in LaOFeAs to 55 K in SmOFeAs. In addition to REOFeAs compounds, AFe_2As_2, LiFeAs and $FeSe_{1-x}$ compounds have also been found,
with similar superconducting and normal state properties.
Their crystal structures show
a common motive, characterized by a square Fe lattice, surrounded by
As(Fe) atoms arranged on distorted tetrahedra.
Besides superconductivity, Fe pnictides show
a spin density wave (SDW) transition accompanied by a lattice distortion.
This points to a possible unconventional origin of superconductivity.
Theoretically, there is no general consensus on the pairing mechanism.
In this talk, I will use Density Functional theory to describe the
electronic and vibrational properties of LaOFeAs, which is a prototype
compound for iron pnictides.
Using linear response calculations,
I will show that the standard Migdal-Eliashberg theory fails to
account for the observed critical temperature.[1]
I will then review some of the DFT results concerning magnetism
in these materials, showing that LDA reproduces the qualitative features
observed by the experiment, but fails quantitatively.[2]
Using an ab-initio effective tight-binding Hamiltonian, based on Fe d and As p
Wannier orbitals, derived from NMTO downfolding,
I will then analyze in detail the origin of the complicated band structure of
iron pnictides. I will then use this tight-binding model to discuss the
origin of magnetism in FeAs and its itinerant nature[3].

[1] L. Boeri, O. V. Dolgov, and A. A. Golubov,

Phys. Rev. Lett. **101**, 026403 (2008).
[2] I. I. Mazin, M. D. Johannes, L. Boeri, K. Koepernik, and D. J. Singh, Phys. Rev. B **78**, 085104 (2008).
[3] O.K. Andersen and L. Boeri, *in preparation*

Hydrogen Superconductivity and other superconductors

Gianni Profeta[1], *P. Cudazzo*[1], *A. Sanna*[2], *A. Floris*[2], *A. Continenza*[1], *S. Massidda*[3], *E. K. U. Gross*[2]

1. CNISM - Dip. di Fisica, Università degli Studi dell'Aquila, Italy,
2. Institut für Theoretische Physik, Freie Universität Berlin, Germany
3. SLACS-INFM/CNR and Dip. di Scienze Fisiche, Univ. di Cagliari, Italy.

The SuperConducting Density Functional Theory (SCDFT) revealed, in the last few years, as an efficient theoretical and computational method for the study of the superconducting properties of real materials.
After a brief review of its predicting power, comparing the theoretical predictions with many experimental accessible quantities (critical temperatures, specific heat, tunneling experiment, isotope effect, etc...) on a wide class of materials, we present the results of SCDFT study on dense molecular hydrogen.
High superconducting critical temperature was predicted on the *Cmca* phase, the stable metallic high pressure structure.
Our study is able to single out the features which drive the system towards multiband-superconductivity: mainly, a rich and complex Fermi surface and strongly coupled phonon modes driving the intra-inter molecular charge transfer. We demonstrate that in this simple system a very high superconducting critical temperature can be reached via electron-phonon and Coulomb electron-electron interactions.

Ab-initio pseudopotential calculations of the orbital magnetization [*]

Davide Ceresoli

Department of Materials Science and Engineering,
Massachusetts Institute of Technology
77 Massachusetts Ave, Cambridge MA 02139, USA

The electric polarization (P) and the orbital magnetization (M) are well known textbook topics in solid state physics. While it is easy to compute their derivatives in an extended system, P and M themselves are not easy to formulate, due to the unboundedness of the position operator. The problem of the electric polarization has been solved in the '90s by the Modern Theory of Polarization (MTP) [1], which relates the electric polarization to the electrons Berry phase.

Only recently, two independent groups found a formula for the orbital magnetization in periodic systems [2]. Since the discovery of the MTP, many papers have appeared reporting successful applications to first principles calculations of dielectric and piezoelectric properties of real materials. However, ab-initio calculations of the orbital magnetization on real materials, by the newly discovered formula, have not been reported in literature so far.

We present first principles calculations of the orbital magnetization by the plane wave pseudopotential method. As an application, we show that the NMR chemical shifts and the EPR g-tensor can now be calculated from the orbital magnetization by a "converse" approach. The advantages of the new approach are: (1) it avoids any linear response calculation, (2) it is not plagued by the gauge-origin problem of most quantum chemistry methods.

Finally, we present results for the orbital magnetization of ferromagnetic Fe, Co and Ni. With respect to muffin-tin methods, our plane wave implementation has the advantage of taking into account also itinerant contribution coming from the interstitial regions.

1. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993); R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
2. T. Thonhauser *et al.*, Phys. Rev. Lett. **95**, 137205 (2005); D. Ceresoli *et al.*, Phys. Rev. B **74**, 024408 (2006); D. Xiao *et al.*, Phys. Rev. Lett. **99**, 197202 (2007).

[*] Work done in collaboration with: U. Gerstmann, A. P. Seitsonen, F. Mauri, T. Thonhauser, N. Marzari, D. Vanderbilt and R. Resta.

First-principles electrochemistry

Ismaila Dabo[1], *Eric Cances*[2], *Yanli Li*[2], *Nicola Marzari*[3]

1. INRIA and Universite Paris-Est
2. Universite Paris-Est
3. MIT

Rising sustainability concerns have revived strong interest in electrochemical electricity generation whose basic principle is to catalytically convert the energy stored in chemical bonds into usable electrical power. Despite recent advances in the application of first-principles simulations to electrochemistry, a comprehensive computational approach to study quantum-mechanical systems at fixed applied voltage had been lacking. In this work, we present a practical method to study electrochemical processes at electrode surfaces under realistic voltage conditions. To validate this method, we calculate the dependence of the vibrational frequencies of chemisorbed molecules as a function of the electrode voltage – the vibrational Stark effect – , finding excellent agreement with electrochemical spectroscopic experiments and resolving previous controversies.

ABSTRACTS OF POSTERS

(in order of topic and presenting author name)

LIST OF TOPICS

Theory and Methods:
T1 Density-Functional Theory beyond LDA
T2 Time Dependent DFT
T3 Many-Body Techniques for Real Materials
T4 Quantum Monte Carlo
T5 Ab-initio Molecular Dynamics
T6 Large Scale and Multiscale Simulations
T7 Activated Processes
T8 Electronic and Thermal Transport
T9 Response to External Fields
T10 Simulations in Realistic Environments
T11 Other methods

Applications:
A1 Nanoscience
A2 Biochemistry and Biomaterials
A3 Magnetism and Spintronics
A4 Geophysics
A5 Functional Materials
A6 Surfaces
A7 Spectroscopies
A8 Catalysis and Electrochemistry
A9 Chemical Reactions and Kinetics
A10 Materials Design
A11 Other applications

T1 Density-Functional Theory beyond LDA

Theoretical study of Group II Bimetallic interfaces, using DFT

Abdalla M. Al-kelsh(1), and Omnia mosa(1)

(1) Physics department, Faculty of Science,
Al-Fateh University, Tripoli, Libya.
alkelsh@yahoo.com

The subjects of metallic surfaces and bimetallic interfaces are of great theoretical and technological importance. It has many applications such as thin films, electrical contacts, etc, and provides a good testing ground for the many– body theories. Therefore, bimetallic systems of Group II were suggested in this study in order to modify an electronic density modules and find their , electric fields, and potentials using DFT. Density Functional Theory (DFT) was applied to calculate the ground state energy of each couple. The total ground state energy is a universal function of electronic density and includes kinetic, electrostatic, exchange, and correlation energies. An approximations has been taken and the Wigner interpolation scheme of correlation energy $(\mathrm{LDFT})_{\mathrm{W}}$ were used in this study. However, our modified theoretical model satisfied all properties and conditions of each system, it proves very good in Group II, as well in Group I, our numerical results of the electronic density, electric filed, potential, agrees within (±10%) with the previous studies. However this can be overcome by using non–local density approximation, (NLDA).

Main Topic: T1 Density-Functional Theory beyond LDA

Intermolecular interaction in DFT : Application to Carbon Nanotubes and Fullerenes.

Y.J. Dappe

Institut de Physique et Chimie des Matériaux de Strasbourg,
23 Rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

J. Ortega and F. Flores

Departamento de Física Teórica de la Materia Condensada,
Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain

Abstract

A theoretical study of weak interactions in graphitic materials like Carbon Nanotubes, Fullerenes and graphene is presented here. Based on a localized orbitals DFT formalism, our treatment which has already been applied for graphene-graphene interaction describes independently the weak chemical as well as the van der Waals interaction with high accuracy. The weak chemical interaction is described in the frame of the LCAO-S2 model based on a weak overlap expansion, and the van der Waals interaction is treated in the dipolar approximation, taking into account virtual transitions of high energy. This formalism is applied here to the case of lateral interaction between CNTs, C60 -dimers, adsorption of C60 on graphene and CNT, and encapsulation of C60 and CNT. The power law of the interaction is analyzed, and useful parameters like C6 coefficient and an exponential model for the chemical interaction are extracted. Beyond the study of graphitic materials, this work opens new perspectives in the analysis of weakly bounded metal/organics interfaces.

---

[1] M.A. Basanta, Y.J. Dappe, J. Ortega and F. Flores, Europhys. Lett. **70**, 355 (2005).

[2] Y.J. Dappe, M.A. Basanta, J. Ortega and F. Flores, Phys. Rev. B **74**, 205434 (2006).

[3] Y.J. Dappe, J. Ortega and F. Flores, submitted to Phys. Rev. B (2008).

Main Topic: T1 Density-Functional Theory beyond LDA

Ab initio calculation of CVV Auger spectra in closed-shell systems

G. Fratesi,[1,2] *M. I. Trioni,*[2] *G. P. Brivio,*[1,2] *S. Ugenti,* [3,4] *E. Perfetto,*[1,5] *and M. Cini*[3,4]

1. Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Italy
2. ETSF and CNISM, UdR Milano-Bicocca, Italy
3. Dipartimento di Fisica, Università di Roma Tor Vergata, Italy
4. Laboratori Nazionali di Frascati, INFN, Frascati, Italy
5. Unità CNISM, Università di Roma Tor Vergata, Italy

We propose an *ab initio* method to evaluate the core-valence-valence (CVV) Auger spectrum of systems with filled valence bands. The method is based on the Cini-Sawatzky theory, and aims at estimating the parameters by first-principles calculations in the framework of density-functional theory (DFT). Photoemission energies and the interaction energy for the two holes in the final state are evaluated by performing DFT simulations for the system with varied population of electronic levels. Transition matrix elements are taken from atomic results. The approach takes into account the non-sphericity of the density of states of the emitting atom, spin-orbit interaction in core and valence, and non quadratic terms in the total energy expansion with respect to fractional occupation numbers. It is tested on two benchmark systems, Zn and Cu metals, leading in both cases to $L_{23}M_{45}M_{45}$ Auger peaks within 2 eV from the experimental ones. Detailed analysis is presented on the relative weight of the various contributions considered in our method, providing the basis for future development. Especially problematic is the evaluation of the hole-hole interaction for systems with broad valence bands: our method underestimates its value in Cu, while we obtain excellent results for this quantity in Zn.

Main Topic: T1 Density-Functional Theory beyond LDA

Pressure-induced structural, electronic and magnetic effects in BiFeO3

O-E Gonzalez-Vazquez[1], *Jorge Iñiguez*[1]

1. Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

This is the text of my abstract.

We present a first-principles study of BiFeO3 at high pressures. Our calculations reveal the main structural (change in bismuth's coordination and loss of ferroelectricity), electronic (spin crossover and metallization), and magnetic (loss of order) effects favored by compression and how they are connected. Our results are consistent with the striking manifold transition observed experimentally by Gavriliuk et al. [Phys. Rev. B 77, 155112 (2008)] and provide an explanation for it.

Note: Please choose one of the following as "Main Topic" above:

Theory and Methods:

T1 Density-Functional Theory beyond LDA

Applications:
A3 Magnetism and Spintronics
A5 Functional Materials
A10 Materials Design

Main Topic: T1 Density-Functional Theory beyond LDA

Influence of Cr doping on the structural and the electronic properties of V_2O_3

Federico Iori, Matteo Gatti, Lucia Reining

European Theoretical Spectroscopy Facility - LSI Ecole Polytechnique, CNRS -CEA-IRAMIS, Palaiseau, France

Aim of our work is to study through ab initio theoretical approach the paramagnetic insulting phase of V_2O_3 compound, in order to understand better the metal-insulator phase transition subdues by V_2O_3 [1, 3].

It has been shown that at DFT level it's not possible to describe properly the insulating paramagnetic phase because of a poor treatment of the strong electronic correlation for such systems with d- or f- incomplete shell. Moreover the comparison of DFT density of state with the experimental one is not possible until including many body effect such the ones arising from a direct photoemission spectroscopy. Within a traditional ab initio density functional scheme, the Kohn-Sham eigenvalues can' t be used for an appropriate description of the electronic bands structures, leading in particulaer for such a system (VO_2, V_2O_3) [2] to an underestimation or even to a closure of the photoemission band gaps [5].

Moreover, from the experimental point of view it has bee shown that adding small amount of Cr into the V_2O_3 a sharp metal-insulator transition arises as a function of both Cr concentration and pression at room temperature. Since to the best of our knowledge all the theoretical calculation present in the literature concern only V_2O_3 without really taking into account the Cr dopant atom [1], we decide to perform ab initio calculation by considering Cr-doped V_2O_3 supercell system in order to point out which role the presence of the dopant plays on the electronic structure during the metal-insulator paramagnetic transition of the V_2O_3 .

References

[1] G. Keller et al., Phys. Rev. B **70**, 205116 (2004)

[2] M. Gatti et al., Phys. Rev. Lett **99**, 266402 (2007)

[3] S.-K. Mo et al., Phys. Rev. Lett. **90**, 186403 (2003)

[4] A. I. Frenkel et al., Phys Rev. Lett. **97**, 195502 (2006)

[5] W. G. Aulbur et al., Solid State Phys. **54**, 1 (1999)

Main Topic: T1 Density-Functional Theory beyond LDA

A Correlation Energy Functional for Exact Exchange Kohn Sham Theory from Reduced Density Matrix Functional Theory.

Nikitas Gidopoulos[1,2] , *Nektarios Lathiotakis*[1], *Nicole Helbig*[3],

1. Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vas. Constantinou 48, GR-11635, Athens, Greece
2. ISIS, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, OX11 0QX, U.K.
3. Nano-Bio Spectroscopy group and ETSF, Dpto. de Física de Materiales, Universidad del País Vasco UPV/EHU and Centro Mixto CSIC-UPV/EHU, San Sebastián, Spain

The total energy in Reduced Density Matrix Functional Theory (RDMFT) is minimized, under the constraint that the natural orbitals (NO's) are the eigenorbitals of a local effective potential. This leads to a significant reduction of computation time to calculate the NO's compared with their direct minimization, and makes the cost of the method comparable to a Kohn Sham calculation using exact exchange. In addition, it offers the opportunity to interpret the eigenvalues of the Hamiltonian built with this potential as the energy spectrum of the system. On the other hand, correlation can be introduced to Exact Exchange (EXX) by keeping the EXX orbitals but minimizing the occupation numbers using various RDMFT functionals. In that way, the introduced correlation energy plays the role of correlation energy functional in Density Functional Theory. Results will be presented on small systems.

Main Topic: T1 Density-Functional Theory beyond LDA

The nonlocal correlation as the solution of the CO puzzle problem

Predrag Lazic[1,4], *Mojtaba Alaei*[2], *Nicolae Atodiresei*[1,3] *Vasile Caciuc*[1] *Radovan Brako*[4] *Stefan Blügel*[1]

1. Institut für Festkörperforschung (IFF) and Institute for Advanced Simulation (IAS), Forschungszentrum Jülich, 52425 Jülich, Germany
2. Department of Physics, Isfahan University of Technology, Isfahan 84156, Iran
3. The Institute of Scientific and Industrial Research, Osaka University, 567-0047 Osaka, Japan
4. Rudjer Bošković Institute, Zagreb, Croatia

For the last 20 years the Density Functional Theory (DFT) has been the standard approach for the calculation of chemisorption, adsorption, chemical reactions and electronic structure in general. Despite the great successes of the theory in predicting adsorption energies and other properties for many systems it turns out that the theory fails to predict correctly the adsorption site preference for the CO molecule on (111) surfaces of Pt, Cu and Rh, for example. The DFT calculations predict that the highly coordinated FCC (hollow) site adsorption is preferred over the top site adsorption, while experiments show unambiguously that CO adsorbs into the top site. Also, the calculated adsorption energies do not match well the experimental values. CO molecule chemisorption on these surfaces is a type of system in which one would expect DFT theory in its present implementation with semi-local (GGA) functionals to work well. Systems for which DFT is not expected to give good results due to the semi-locality of the energy functionals are those in which physisisorption dominates over chemical bonding, i.e. typical van der Waals systems. However, van der Waals is specific name for a more general phenomenon, the nonlocal correlation. We show that the inclusion of the nonlocal correlation in its most general "seamless" formulation into the DFT calculations of CO chemisorption largely solves the discrepancies known as the CO puzzle problem.

Main Topic: T1 Density-Functional Theory beyond LDA

First-principles study of high-temperature ferroelectric $La_2Ti_2O_7$

Jorge López-Pérez and *Jorge Íñiguez*

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)
Campus UAB, 08193 Bellaterra, Spain

We have used first-principles methods to study the origin of the very high Curie temperature of $La_2Ti_2O_7$, a layered perovskite that remains ferroelectric up to about 1770 K. Our work reveals that the nature of the ferroelectricity in $La_2Ti_2O_7$ differs greatly from what is typical in prototypical ferroelectric compounds like $BaTiO_3$ or $PbTiO_3$. In $La_2Ti_2O_7$, ferroelectricity results from a structural transition that involves concerted rotations of the oxygen octahedra, as the layering of the structure makes it possible for such rotations to produce a finite polarization, something that cannot occur in a perfect perovskite lattice. Hence, the case of $La_2Ti_2O_7$ illustrates a novel physical mechanism, based on the topology of the crystalline lattice, that can lead to ferroelectricity at very high temperatures.

Main Topic: T1 Density-Functional Theory beyond LDA

A first-principles investigation of structural, elastic, electronic and optical properties of the ABO_3 perovskite-type crystal

S. K. Medeiros[1], E. L. Albuquerque[2], F. F. Maia Jr.[3], V. N. Freire[3]

1. Departamento de Física, Universidade do Estado do Rio Grande do Norte, 59610-210 Mossoró, Rio Grande do Norte, Brazil.
2. Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, 59072-970 Natal, Rio Grande do Norte, Brazil.
3. Departamento de Física, Universidade Federal do Ceará, Caixa Postal 6030, 60455-900 Fortaleza, Ceará, Brazil.

First principles study of structural, elastic, electronic and optical properties of the cubic perovskite-type $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, $NaNbO_3$, $PbTiO_3$, $PbZrO_3$ and $BaZrO_3$ have been reported by density functional theory (DFT) calculations, using the pseudo-potential plane wave method within the local density (LDA) and generalized gradient (GGA) approximations, determining several properties, *e. g.*, lattice parameters, bond length, electrons density, energy band structures, electrons density of states, effective masses and optical properties, such as, dielectric function, absorption coefficient, optical reflectivity, refractive index, extinction coefficient, conductivity, and electron energy loss. The dynamics and potential energy curves of cubic perovskite as a function of lattice volume also were investigated. The elastic constants and their pressure dependence are calculated using the static finite strain technique. A linear pressure dependence of the elastic stiffnesses is found. The variation of the gap versus pressure is well fitted to a quadratic function. The results equilibrium lattices are in a reasonable agreement with the previous experimental predictions. However, many of the results presented in this work still awaits experimental confirmation. Those results will be employed to investigate the confinement of excitons in spherical quantum dots.

Main Topic: T1 Density-Functional Theory beyond LDA

Linear Scaling DFT+U with ONETEP

David D. O'Regan[1], *Arash A. Mostofi*[2], *Mike C. Payne*[3]

1. Cavendish Laboratory, University of Cambridge, United Kingdom
2. The Thomas Young Centre, Imperial College London, United Kingdom
3. Cavendish Laboratory, University of Cambridge, United Kingdom

ONETEP is an ab initio total-energy and force code for which the required computational effort scales linearly with the number of atoms in the simulation cell[1][2]. ONETEP has recently been shown to scale up to systems consisting of 32,000 atoms on as few as 64 cores[3]. This opens the way to first-principles calculations that are able to include the protein structure and solvation medium surrounding an enzymatic site or chromophore of biological macromolecule.

Standard exchange and correlation functionals are unable to describe the electronic structure of many such systems correctly, due to a tendency to underlocalise electronic states associated with the transition metal centres. The DFT+U method[4][5] is a simple, computationally inexpensive technique which augments the description of on-site Coulomb interactions offered by standard functionals, cancelling part of the spurious self-interaction and thereby extending their range of reliable applicability.

We present a parallelised implementation scheme for the DFT+U exchange-correlation correction in ONETEP which is fully self-consistent over the charge density, Hubbard projectors and U interaction parameters. The method described is generally applicable to density-matrix methods which employ a non-orthogonal basis set.

---

[1] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi, M. C. Payne, *J. Chem. Phys.* **122** 084119 (2005)

[2] P. D. Haynes, C.-K. Skylaris, A. A. Mostofi and M. C. Payne, *Phys. Status. Solidi b* **243** 2489 (2006)

[3] N. D. M. Hine, P. D. Haynes, A. A. Mostofi, C.-K. Skylaris and M. C. Payne, submitted to *J. Chem. Phys.* (2008)

[4] V. I. Anisimov, J. Zaanen, O. K. Andersen. *Phys. Rev. B* **44** 943 (1991)

[5] V. I. Anisimov, F. Aryasetiawan, A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9** 767 (1997)

Main Topic: T1 Density-Functional Theory beyond LDA

An approach to systematic error estimation for DFT

Vivien Petzold, Thomas Bligaard, Carsten Rostgaard, Jens K. Nørskov, and
Karsten W. Jacobsen

Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark

Density functional theory (DFT) calculations have become an essential tool for the research within solid state physics and chemistry. However, currently many different approximations exist to the exchange-correlation functional varying not only in the type of physics described but also in the detailed implementation. As a result many “standard” functionals exist today which are more appropriate for some class of materials than for others. Experienced practitioners of DFT know this very well but it is our aim to develop a general scheme to assess the validity of a certain DFT implementation by providing realistic error estimates on predicted quantities. We furthermore aim to construct optimal functionals within certain classes of functionals (GGAs, hybrids etc).

Using ideas from Bayesian statistics we have thus constructed an ensemble of GGA functionals with the aim of providing realistic error bars for calculations with the RPBE functional on molecules and chemisorption systems. We have furthermore constructed a GGA-functional which is optimal for describing molecular properties at present in the G2 database. The functional is seen to predict molecular atomization energies with an accuracy comparable to standard hybrid functionals but at a much lower computational cost.

Main Topic: T1 Density-Functional Theory beyond LDA

Properties of the coupling-strength integrated exchange-correlation hole in DFT

Mats-Erik Pistol

Solid State Physics, Lund University, Box 118, Sweden

We have investigated the coupling-strength integrated exchange-correlation hole in density functional theory. We demonstrate that the exchange-correlation hole belongs to a convex set, if the electron density is fixed. Using this information we show that the coupling-strength integrated exchange-correlation hole obeys the same N-representability conditions as the non-integrated exchange-correlation holes obeys. In order to show these things we first note that the pair densities that can be obtained from a wave-function, i. e. that are N-representable, belong to a convex set, P[N]. From this we can show that the exchange-correlation hole also belongs to a convex set, Q[N,n], if the electron density is fixed (and also if the electron density is not restricted). Since the electron density is fixed, when doing the adiabatic connection, it follows easily that the coupling strength integrated exchange-correlation hole belongs to the same set, Q[N,n] as the non-integrated holes. However we can also argue that the correct set that the exchange-correlation hole belongs to, is in fact a subset of Q[N,n]. We give two rules, not usually employed in density functional theory, that the exchange-correlation hole must obey. The first rule is that a certain Hilbert-Schmit kernel integral kernel, derived from the exchange-correlation hole, is a positive definite operator. The second rule comes from the observation that N-representable distance densities have positive Fourier transforms.

Main Topic: T1 Density-Functional Theory beyond LDA

Lattice vibration spectrum of ScN from first-principles calculations

S. Saib [1], *N. Bouarissa* [2], *P. Rodríguez-Hernández* [3] *and A. Muñoz* [3]
1.Department of Physics, Faculty of Science, Msila University, Msila 28000, Algeria
2.Departamento de Fisica Fundamental II, Universidad de La Laguna, La Laguna
E-38205, Tenerife, Spain
3.Department of Physics, Faculty of Science, King Khalid University, Abha, P.O.Box
9004,Saudi Arabia

Abstract

We report first-principles calculations in the frame work of the density functional perturbation theory of the lattice vibration properties of ScN in the wurtzite and rocksalt phases at zero and under pressures ranging from 0 to 40 GPa. The calculations predict the full phonon spectrum throughout the Brillouin zone and phonon density of states. Generally, the calculated zone-center modes for wurtzite structure are found to be in good agreement with previous theoretical and experimental results. The pressure dependence of the zone-center optical frequencies is examined and discussed which allowed the calculation of the pressure coefficients and mode Grüneisen parameters.

Main Topic: T1 Density-Functional Theory beyond LDA

Studying electron transfer using constrained density functional theory.

Alex M P Sena[1,2], David R Bowler[1,2]

1. London Centre for Nanotechnology
2. Department of Physics and Astronomy, University College London

The study of electron transfer (ET) is important both because of the fundamental role it plays in important biological processes such as photosynthesis and respiration, but also because it is an important aspect of the workings of potential molecular electronic components such as nanowires or molecular memories. Density functional theory (DFT) is often unable to correctly describe the states of localized charge involved in ET, due to a phenomenon known as the self-interaction error which results in overly delocalized charge distributions. Partial solutions to this problem, such as more sophisticated exchange-correlation functionals (B3LYP) and more sophisticated methods (GW approximation) exist. However, they are often prohibitively expensive to use.

Constrained density functional theory (cDFT) is another solution to this problem, which has recently been reformulated in an efficient framework. In cDFT, an extra term is added to the Hamiltonian, to impose a desired condition on the system's charge distribution. The constraint is formulated in terms of atomic populations (Löwdin analysis) and can be optimized efficiently within a Lagrange multiplier framework. By using cDFT to obtain the states of localized charge, the reorganization energy of an ET process can be calculated.

In this work, cDFT is implemented within the order(N) DFT code CONQUEST. Some initial calculations on charge separated systems are demonstrated and the improvements over conventional DFT calculations outlined. Eventually, the computational study of ET processes in large biological systems, should be possible with this method.

Main Topic: T1 Density-Functional Theory beyond LDA

The ground state properties of 3C-SiC using density functional theory

B. Y. Thakore
Department of Physics, Sardar Patel University
Vallabh Visyanagar-388120, Gujarat State, INDIA

A comprehensive theoretical study on structural, elastic and vibrational properties of zincblende Silicon carbide (SiC) compound is made using the plane wave self consistent method in the frame work of density functional theory. Both the linear density approximation (LDA) and the generalized gradient approximations (GGA) are used as the exchange-correlations. The ultrasoft pseudopotentials are employed which treats only valance electrons explicitly. The high pressure phase transition from zincblende to rocksalt crystal structure is successfully estimated. Calculated equilibrium properties such as lattice constant, bulk modulus and elastic constants are in good agreement with experimental and other theoretical studies. The vibrational properties are also computed and matched with recently published experimental work. Since the material has large number of industrial applications the equation of state generated will be very useful.

Keywords: Density Functional Theory, Phase transition, Zincblende, Rocksalt

Main Topic: T1 Density-Functional Theory beyond LDA

Numerical evaluation of four-center integrals for pseudo-atomic orbitals

Masayuki TOYODA *and Taisuke OZAKI*

Research Center for Integrated Science, Japan Advanced Institute of Science and Technology, 1-1, Asahidai, Nomi, Ishikawa 932-1292, Japan.

A computation program has been developed to calculate the four-center electron repulsion integrals (ERI) where the numerical pseudo-atomic orbitals (PAO) are used as the basis functions. With this program, the Hartree-Fock-type (so-called "exact") exchange can be calculated for the local basis functions in the first-principles calculations based on the density-functional theory. The mathematical procedure for the numerical integration of the ERI has been proposed by Talman [1]. Unlike the analytic basis functions which have been tested in Talman's work, the PAO basis functions have cut-off radii which cause numerical difficulties in the spherical Bessel transforms. We performed a careful investigation of the routines for the numerical spherical Bessel transforms of PAOs. We found that the fast Spherical Bessel transform method by Siegman [2] and Talman [3] with simple correction in the small-r (or k) region works quite effectively in both terms of the computation speed and accuracy. In the paper, we show the values of the ERI for some simple molecules with PAO basis functions. The PAO data is taken from those of the first-principles calculation program OpenMX [4, 5]. The accuracy of the values is controlled by the number of radial mesh points N and the cut-off angular momentum for summation $L_{\max}$. The convergence in energy up to 10^{-5} Hartree is successfully obtained with $N \sim 1000$ and $L_{\max} \sim 15$.

[1] J. D. Talman, Int. J. Quantum Chem. **93** 72 (2003).
[2] A. E. Siegman, Optics Lett. **1**, 13, (1977).
[3] J. D. Talman, J. Comput. Phys. **29**, 3 (1978).
[4] T. Ozaki and H. Kino, Phys. Rev. B **69**, 195113 (2004) ;*ibid.* **72**, 045121 (2005).
[5] http://www.openmx-square.org/

Main Topic: T1 Density-Functional Theory beyond LDA

Ab-initio calculation of the phonon dispersion relations of lead chalcogenides

Ludger Wirtz[1], *Ondrej Kilian*[1], *Guy Allan*[1]

1. Institute for Electronics, Microelectronics, and Nanotechnology
CNRS UMR 8520, Dept. ISEN,
B.P. 60069, 59652 Villeneuve d'Ascq Cedex, France

We present *ab-initio* phonon dispersion relations for the three lead chalcogenides PbS, PbSe, and PbTe. The acoustic branches are in very good agreement with inelastic neutron-scattering data. The pronounced minimum of the transverse optical branch at Γ due to the near-ferroelectricity of the lead chalcogenides is qualitatively reproduced. In addition, we find a pronounced kink in the longitudinal optical branch at Γ. This kink was previously explained as the effect of "free carriers". Our calculations, however, demonstrate that this anomaly is also present in the pure lead chalcogenides. We explain this kink as a "near" Kohn-anomaly due to the peculiar electronic band-structure: The lead chalcogenides have a narrow direct gap (200-300 meV) at the high symmetry point L. The gap strongly depends on the lattice constant. By (artificially) squeezing the lattice one can reduce the gap to zero and obtain a linear crossing of the conduction and valence band at L. In this case, LO and TO modes are degenerate and the LO mode displays a Kohn-Anomaly in analogy to the case of graphene with its point-like Fermi-surface.

Main Topic: T1 Density-Functional Theory beyond LDA

Corannulene on Cu(111) surface: structure and properties using a first-principle theoretical approach

Laura Zoppi[1]*, Kim Baldridge*[1]*, Alberto Garcia*[2]

1. Organic Chemistry Institute, University of Zürich, Winterthurerstrasse 190, 8050 Zürich
2. Institut de Ciencia de Materials de Barcelona – CSIC, Campus de la UAB, E-08193 Bellaterra (Barcelona), Spain.

The interaction of curved aromatic carbon surfaces with metal atoms represents an area of broad interest in organometallic chemistry. The intriguing question regarding the preference for metal binding to the concave versus convex side has been investigated both theoretically and experimentally, most notably focusing on Corannulene $C_{20}H_{10}$ (COR) [1] as prototype system. In this work, we study the specific case of COR adsorption on Cu(111) surface. The interest in this system stems from recent STM experimental findings [2] which shows that COR adsorbed on Cu(111) gives rise to very peculiar supramolecular aggregation processes. In order to elucidate the fundamental mechanisms involved, we adopt a first principle electronic structure approach by adding to a standard DFT-GGA framework a sempiempirical term taking into account dispersions contributions [3], employing the SIESTA code. This is a typical case where DFT, both at LDA and GGA level, totally fails due to the weak character of the interactions involved. Structural relaxations of a single COR molecule located on top of the high symmetry sites of a six-layer Cu(111) slab (~ 400 atoms) are performed. Subsequently, electronic structure analysis focused on the charge rearrangement at the surface-molecule interface is performed. From this analysis, the deformation dipole and the work function modification upon molecule adsorption are also gained. Such investigation turns out to be crucial in elucidating the binding mechanism of the molecule to the surface.

[1] T. J. Seiders; K. K. Baldridge, ; J. M. O' Connor; J. S. Siegel, JACS, **119**, 4781 (1997)

[2] K. H. Ernst et al., submitted to Angew. Int. Chem. Ed.

[3] S. Grimme, J. Comp. Chem., **27**, 1787 (2006)

Main Topic: T2 Time Dependent DFT

Time Dependent DFT study of the photo-excitation of a light-harvesting supramolecular triad

N. Spallanzani[1,2], *C. A. Rozzi*[2], *D. Varsano*[2,3], *F. Manghi*[1,2], *A. Rubio*[3,4]

1. Dipartimento di Fisica, Università di Modena e Reggio Emilia, Modena, Italy
2. INFM-CNR National Research Center "S3", Modena, Italy
3. European Theoretical Spectroscopy Facility (ETSF)
4. Departamento de Física de Materiales, Universidad del Pais Vasco, San Sebastián, Spain

Bioinspired light-harvesting materials are very promising candidates for high efficiency photovoltaic devices. The key of their efficiency is the built-in photoinduced charge separation mechanism. We provide a first-principles description of optical properties, based on Time-Dependent Density Functional Theory (TDDFT), of a light-harvesting Carotenoid-Dyaril-Porphyrin-C_{60} molecular triad. We show that TDDFT is able to accurately describe the optical absorption and polarizability of a such large system. We have calculated the photoabsorption cross section, and we have found good agreement with experimental data. We provide an interpretation of the photo-excitation mechanism in terms of the properties of the component moieties.

Main Topic: T3 Many-Body Techniques for Real Materials

Melting properties of a simple tight-binding model of transition metals: The region of half-filled *d*-band

C. Cazorla[1,2,3]*, D. Alfe*[1,2,3,4]*, and M. J. Gillan*[1,2,3]

1. Materials Simulation Laboratory, London WC1E 6BT, U.K.
2. London Centre for Nanotechnology, UCL, London WC1H 0AH, U.K.
3. Dept. of Physics and Astronomy, UCL, London WC1E 6BT, U.K.
4. Dept. of Earth Sciences, UCL, London WC1E 6BT, U.K.

Over the last five years, there has been a vigorous controversy over the high-pressure melting curves of transition metals. The melting temperatures derived from shock experiments and static-compression experiments on some bcc metals differ by several thousand K in the Mbar region. Earlier first-principles simulations [1,2,3,4] support the shock data. In order to gain further insight, we have calculated the free energy, and hence the melting properties, of a simple tight-binding model for transition metals in the region of d-band filling near the middle of a d-series, the parameters of the model being designed to mimic molybdenum. The model is intended to be the simplest possible tight-binding representation of the two basic parts of the energy: first, the pairwise repulsion due to Fermi exclusion; and second the d-band bonding energy described in terms of an electronic density of states that depends on structure. In addition to the number of d-electrons, the model contains four parameters, which are adjusted to fit the pressure dependent d-band width and the zero-temperature pressure-volume relation of Mo. We show that the resulting model reproduces well the phonon dispersion relations of Mo in the body-centred-cubic (bcc) structure, as well as the radial distribution function of the high-temperature solid and liquid given by earlier first-principles simulations. Our free-energy calculations start from the free energy of the liquid and solid phases of the purely repulsive pair-potential model, without d-band bonding. The free energy of the full tight-binding model is obtained from this by thermodynamic integration. The resulting melting properties of the model are quite close to those given by earlier first-principles work on Mo.

[1] C.Cazorla, M. J. Gillan, S. Taioli and D. Alfe, J. Chem. Phys. **126**, 194502 (2007)

[2] S. Taioli, C. Cazorla, M. J. Gillan and D. Alfe, Phys. Rev. B **75**, 214103 (2007)

[3] A. B. Belonoshko *et al.,* Phys. Rev. Lett. **100**, 135701 (2008)

[4] C. Cazorla, D. Alfe and M. J. Gillan, Phys. Rev. Lett. **101**, 049601 (2008)

Main Topic: T3 Many-Body Techniques for Real Materials

Exciton–plasmon states in nanoscale materials: breakdown of the Tamm–Dancoff approximation

Myrta Grüning[1], *Andrea Marini*[2], *Xavier Gonze*[1]

1. European Theoretical Spectroscopy Facility (ETSF), PCPM, Université Catholique de Louvain, 1, place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium
2. European Theoretical Spectroscopy Facility (ETSF), CNR-INFM Institute for Statistical Mechanics and Complexity, CNISM and Dipartimento di Fisica, Universitá di Roma "Tor Vergata", via della Ricerca Scientifica 1, 00133 Roma, Italy

Within the linear response regime, *ab initio* approaches describe excitons and plasmons as packets of electron-hole pairs. For nanoscale materials, the large number of pairs needed imposes the use of the Tamm-Dancoff approximation, where electron-hole pairs are assumed to move only forward in time. In this work we show that such an approximation can lead to errors as big as the accuracy claimed in *ab initio* calculations. Instead, we propose a general and robust approach to cope with pair-antipair interaction. As an application we calculate *ab initio* the lateral absorption of large carbon nanotubes, and the dynamical polarizability of *trans*-azobenzene.

Main Topic: T3 Many-Body Techniques for Real Materials

Optical spectra and Band Structure of Anatase and Rutile TiO_2

A. Greuling[1], *M. Kaczmarski*[1], *M. Rohlfing*[1],

1. Department of Physics, University of Osnabrueck, Barbarastrasse 7, 49069 Osnabrueck, Germany

TiO_2 is a semiconductor, which is used in many applications. For instance, it is used in biotechnology, cosmetic industry, paint industry, in catalysis or photocatalysis. Therefore, the (optical) properties of TiO_2 are of great interest. As these are still not fully understood in theory we are interested in describing optical spectra with ab initio methods beyond DFT.

We present our results of first principles calculations for Anatase und Rutile TiO_2. Starting from the electronic ground state, which is calculated with DFT(LDA), we describe the single particle excitations with an GWA approach. For both calculations we use a gaussian basisset, because this results in a reasonable computational cost. Then we calculate the electron-hole interaction and solve a Bethe-Salpeter Equation (BSE) in order to get the coupled electron-hole excitations. Based on the resulting data we obtain optical spectra and compare them with experimental data.

Main Topic: T3 Many-Body Techniques for Real Materials

RPA lattice constants and atomization energies

Judith Harl[1], *Georg Kresse*[1],

1. University of Vienna, Sensengasse 8/12, 1090 Vienna, Austria

Density functional theory (DFT) applying the LDA or GGA for the description of the exchange-correlation energy provides an efficient method for a wide range of applications. Nevertheless, errors in the bond length are of the order of 1 % and atomization energies are not reproduced with chemical accuracy (1 kcal/mol). Furthermore, the (semi-)local LDA and GGA do not properly account for long-range van der Waals interactions.

Therefore, the adiabatic connection fluctuation dissipation theorem (ACFDT), which links the electron correlation to the response function and provides, in principle, an exact expression for the correlation energy, has received increased interest in the recent years (e.g., [1]-[3]). In the present work, we evaluate lattice constants and atomization energies of molecules and extended systems within the ACFDT framework applying the random phase approximation (RPA). The RPA routines have been implemented in the Vienna Ab-initio Simulation Package (VASP), a plane wave basis set code.

The RPA energy includes the exact exchange energy and a compatible correlation energy that also accounts for long-range van der Waals interactions. We found that atomization energies and lattice constants of the rare-gas solids Ne, Ar, and Kr are improved compared to LDA and GGA and the correct long-range $1/V^2$ volume dependence could be reproduced [3]. For insulators and metals, covalent and ionic bonded systems, RPA lattice constants are found to deviate on average by only 0.25 % from experiment. Atomization energies, however, are throughout too small ($\approx$ 0.2 eV/atom) and the mean error remains close to the one obtained with DFT-PBE.

[1] F. Furche, Phys. Rev. B **64**, 195120 (2001). [2] A. Marini, P. García-González, A. Rubio, Phys. Rev. Lett. **96**, 136404 (2006). [3] J. Harl, G. Kresse, Phys. Rev. B **77**, 045136 (2008).

Main Topic: T3 Many-Body Techniques for Real Materials

Structural relaxation due to electronic correlations in the paramagnetic insulator $KCuF_3$

I. Leonov[1], *N. Binggeli*[2,3], *Dm. Korotin*[4], *V. I. Anisimov*[4], *N. Stojić*[5,3], *and D. Vollhardt*[1]

1. TP III, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany
2. Abdus Salam International Center for Theoretical Physics, 34014 Trieste, Italy
3. INFM-CNR Democritos, 34014 Trieste, Italy
4. Institute of Metal Physics, 620219 Yekaterinburg GSP-170, Russia
5. International School for Advanced Studies, SISSA, 34014 Trieste, Italy

We present a computational scheme for the investigation of complex materials with strongly interacting electrons which is able to treat atomic displacements, and hence structural relaxation, caused by electronic correlations [1]. It combines *ab initio* band structure and dynamical mean-field theory and is implemented in terms of plane-wave pseudopotentials. Results obtained for paramagnetic $KCuF_3$, namely an equilibrium Jahn-Teller distortion of 4. 2% and antiferro-orbital ordering, agree well with experiment. The electronic correlations are also found to be responsible for a considerable enhancement of the orbital polarization. The GGA+DMFT scheme presented here opens the way for fully microscopic investigations of the structural properties of strongly correlated electron materials such as lattice instabilities observed at correlation induced metal-insulator transitions.

[1] I. Leonov, N. Binggeli, Dm. Korotin, V. I. Anisimov, N. Stojić, and D. Vollhardt, Phys. Rev. Lett. 101, 096405 (2008)

Main Topic: T3 Many-Body Techniques for Real Materials

Excited states of the chromophores within many-body perturbation theory

Yuchen Ma, *Michael Rohlfing*

Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

The excited states of chromophores (photoactive yellow protein chromophores and schiff-base retinal chromophores) are studied using *ab-initio* many-body perturbation theory (GW approximation and Bethe-Salpeter equation), including electronic exchange, correlation, and electron-hole interaction effects. Calculation beyond the Tamm-Dancoff approximation is needed for an accurate description of the lowest excitations, which affects the excitation energy by 0.4 eV. The huge exchange interaction between the electron and hole leads to the unnegligible coupling between the resonant transition and the antiresonant counterpart. Accurate description of the lowest n excitation requires inclusion of the dynamics effect in the electron-hole screening.

Main Topic: T3 Many-Body Techniques for Real Materials

2^{nd}-order Møller-Plesset perturbation theory applied to extended systems

Martijn Marsman, Andreas Grüneis, and Georg Kresse

Faculty of Physics and Center for Computational Materials Science, University Vienna.

The use of wave function based methods, such as Møller-Plesset perturbation theory [1], to add electronic correlation to the Hartree-Fock (HF) approximation is common practice in the computational quantum chemistry of molecular systems. However, due to the computational cost involved—especially when using canonical one-electron wave functions—these methods are not commonly applied to extended systems.

We have implemented 2^{nd}-order Møller-Plesset (MP2) perturbation theory within the framework of the full-potential Projector-Augmented-Wave (PAW) [2] method, using periodic boundary conditions and a plane wave basis set. Important computational aspects of PAW HF+MP2 calculations using a plane wave basis set, most notably the basis set extrapolation of the MP2 correlation energy, will be addressed.

We apply our MP2 implementation to calculate the electronic correlation energy in several archetypical semiconducting and insulating solid state systems. To characterize the accuracy of this level of theory, HF+MP2 lattice constants, bulk moduli, band gaps, and atomization energies are compared to those from density functional theory calculations and experiment. Compared to HF, HF+MP2 yields an improved description of the aforementioned structural properties. Additionally, we demonstrate that HF+MP2 provides a very reasonable description of the van der Waals interactions in extended noble gas solids.

[1] Chr. Møller and M. S. Plesset, "Note on an Approximation Treatment for Many-Electron Systems," Phys. Rev. **46**, 618 (1934).
[2] P. E. Blöchl, "Projector augmented-wave method," Phys. Rev. B **50**, 17953 (1994).

Main Topic: T3 Many-Body Techniques for Real Materials

Physisorption of Organic Molecules on Noble-Metal Surfaces

Michael Rohlfing[1], *Thomas Bredow*[2]

1. Department of Physics, Universität Osnabrück, Germany
2. Institute for Physical and Theoretical Chemistry, Universität Bonn, Germany

We discuss the physisorption of organic molecules to noble-metal surfaces due to Van-der-Waals interaction. Different from density-functional theory, we treat the exchange energy explicitly and calculate the correlation part within the random-phase approximation. In here, the response of the metal surface is described by a combination of a jellium surface and local polarizability of the d electrons, while the response of the adsorbate is obtained from a DFT calculation. We discuss results for the adsorption of Xe, benzene, and PTCDA on the Ag(111) surface. The obtained adsorption energies and distances are between those of DFT-LDA (which overbinds) and DFT-PBE (which does not bind at all), thus constituting a significant improvement beyond DFT.

Main Topic: T3 Many-Body Techniques for Real Materials

MP2 Based on Numeric Atomic Orbitals: Efficient Treatment of Weakly Bonded Systems

Andrea Sanfilippo[1], [3] *XinguoRen*[1] *PatrickRinke*[1,2] *VolkerBlum*[1] *KarstenReuter*[1] *AlexandreTkatchenko*[1] *MatthiasScheffler*[1]

1. Fritz-Haber-Institut, Faradayweg 4-6, D-14195, Berlin
2. Materials Research Lab, University of California at Santa Barbara

Present-day exchange-correlation (xc) functionals in density-functional theory (DFT) are known to be challenged when it comes to an accurate treatment of weak bonding interactions. Second-order Møller-Plesset perturbation theory (MP2) is one of the computationally cheapest methods that can e.g. account for vdW interactions. For ground-state total energy calculations numeric atomic orbitals (NAOs) are known to be an even more efficient basis set choice, in particular when it comes to the treatment of heavier elements. NAO-based MP2 provides a viable alternative route to tackle large systems, considering that modern resolution of identity techniques also enable a competitive numerical ERI evaluation. In order to explore this possibility we have implemented MP2 into the NAO-based in-house computer code “FHI-Aims”. Employing a test set of atoms, as well as covalently, hydrogen-bonded and dispersion-bonded systems we systematically investigate the convergence of the MP2 correlation energy and energy differences with NAO basis sets, that are significantly smaller than corresponding Gaussian ones, thereby paving the way for efficient calculations of large-scale weakly bonding systems. We have therefore applied an exchange correlation scheme to study more challenging systems like graphene and graphite monolayers.

Main Topic: T3 Many-Body Techniques for Real Materials

Electronic properties of carbon based nanostructures from GW calculations

Simone Taioli[1], *Paolo Umari*[2], *Merlyne De Souza*[3]

1. Center for Materials and Microsystems, Via Sommarive 18, 38100 Trento, ITALY
2. SISSA/DEMOCRITOS, Strada Statale 14, 34012 Trieste, ITALY
3. Department of Electrical and Electronic Engineering, The University of Sheffield, Mappin Street, S13JD, Sheffield, United Kingdom

A general description of the electronic properties of model zig-zag carbon nanotubes (CNTs) and chiral-edge graphene nanoribbons using a new computational method for accelerating first-principles Green's functions calculations is presented. The electronic structures and the equilibrium geometries were obtained within the pseudopotential implementation of ab initio total energy DFT. Accurate calculations to determine quasiparticle excitations in carbon nanostructures, notably electronic band gap, are performed in the framework of the GW treatment of the self-energy. Good agreement with previous theoretical results on band gap of the (8,0) carbon nanotube at Gamma point and new model calculations on nanoribbons with edges irregularities show the potential of this method to perform accurate calculations on carbon-based systems of technological interest, otherwise difficult to address with conventional approaches. Furthermore, this technique may be used as a predictive tool of spectral properties, excited states and optical response of carbon based materials in extended systems.

Main Topic: T4 Quantum Monte Carlo

Melting of iron at Earth's core conditions from quantum Monte Carlo free energy calculations

D. Alfè[1] *and E. Sola*[1]

1. Department of Earth Science and Materials Simulation Laboratory, UCL, Gower Street, WC1E London, UK

The Earth's core is formed by an inner part of almost pure solid iron, surrounded by a shell liquid iron which extends roughly half way towards the surface of the planet. The temperature at the centre of the Earth is a crucial parameter in building models for its thermal structure, yet it is impossible to measure. Indirect information can be gathered by exploiting the presence of a solid/liquid boundary (the ICB), which implies that the temperature at this boundary must be the melting temperature. Experiments on the melting of iron under these conditions (pressure of 330 GPa and temperatures in excess of 6000 K) are extremely challenging, and it is not surprising that a large variability of data is found in the literature.

Numerous attempts have been made to calculate the melting temperature of iron using various flavours of approximations to quantum mechanics, the most notable ones employing density functional theory. Here we present new data obtained with quantum Monte Carlo simulations, which show that the temperature of iron at Earth's core conditions is ~ 6800 K, only a few hundred degrees higher that that obtained using density functional theory.

Main Topic: T4 Quantum Monte Carlo

Wavefunction Shift in Diffusion Monte Carlo for Fermionic Systems

Nazım Dugan[1], *İnanç Kanık*[1], *Şakir Erkoç*[1]

1. Middle East Technical University, Physics Department

Quantum Monte Carlo methods suffer from the fermion sign problem when fermionic systems are considered and therefore it becomes an approximate method because of the necessity of the fixed-node approximation. In the current study, new developments on the diffusion Monte Carlo (DMC) method are being researched in order to make it applicable to fermionic systems without fixed-node approximation. Self repeating property of fermionic wavefunctions are being used to limit configuration space in a permutation cell defined by particle exchanges. First space coordinates of the particles are sorted in the beginning and they remain sorted through out the computation. Suitable boundary conditions are applied when these space coordinates of the particles become unsorted. Boundary condition is antisymmetric when odd number of coordinate swaps are necessary to make it ordered and it is symmetric if the number of necessary coordinate swaps is even. In the pure DMC, wavefunction should have constant sign but it changes sign in the permutation cell used in current computations. An upward shift to the wavefunction is applied in order to overcome this problem by a substitution of $(\Psi - A)$ for Ψ in the Schrodinger equation, A being a positive constant whose value is determined according to the permutation cell volume and number of walkers in the DMC simulation. With this substitution at hand, derivative terms becomes unaffected but branching term of the DMC needs to be modified accordingly since potential energy part of the equation becomes $V(\Psi - A)$. Wavefunction value Ψ at the walker position is needed for this modified branching in order to calculate branching probability and it is calculated as the density of walkers about the walker position. The method described above is being tested on the first triplet state of Helium which is the ground state for two same spin electrons in the external potential of nucleus. Current results which comprise wavefunction cross-sections and total energies will be presented and compared with exact results known for the Helium triplet state.

Main Topic: T4 Quantum Monte Carlo

Benchmark DMC calculations of the kinetik, interaction and total energy of the homogeneous electron gas

I. G. Gurtubay[1,2], *R. Gaudoin*[2], *J. M. Pitarke*[1,3]

1. Materia Kondentsatuaren Fisika Saila, Zientzia eta Teknologia Fakultatea,
Euskal Herriko Unibertsitatea, 644 Posta kutxatila, E-48080 Bilbo,
Basque Country, Spain.
2. Donostia International Physics Center (DIPC), Manuel de Lardizabal Pasealekua,
E-20018 Donostia, Basque Country, Spain.
3. CIC nanoGUNE Consolider and Centro de Física Materiales CSIC-UPV/EHU,
Mikeletegi Pasealekua 56, E-20009 Donostia, Basque Country, Spain.

We report DMC energies of a homogeneous electron gas with r_s=2 using the model periodic Coulomb (MPC) interaction and backflow wave functions for N=54,102,178, and 226 electrons. We remove finite size errors by extrapolation and we find lower energies than previously reported. Using the Hellman-Feynmann operator sampling method described in Phys. Rev. Lett. **99**, 126406 (2007) we have computed the exact interaction energy and we have found that the fixed-node error in the interaction energy is one order of magnitude larger than the fixed-node error in the kinetic energy. This opens a way of using the kinetic energies obtained using this method to construct kinetic energy functionals for density functional theory.

P 0033

T4 Quantum Monte Carlo

Numerical simulation of quantum information transfer from squeezed light to □-atom medium by Monte Carlo wave-function method

A. J. Gelman[1], *V. A. Mironov*[1]

[1]Institute of Applied Physics, RAS, Nizhniy Novgorod, Russia,
gelman@appl.sci-nnov.ru

Recent advances in quantum information science have led to many interesting new concepts such as quantum computation, quantum cryptography, and teleportation. The practical implementation of quantum processing protocols requires effective methods of storage and transfer of information, quantum memory. One of the biggest challenges on this way is the dissipation processes in systems which are considered for quantum communication protocols implementation. Dissipation causes fluctuations and quantum noise and can dramatically affect the dynamic of the system. Two main approaches to investigate this problem analytically are the density operator method and Heisenberg-Langevin method. Both methods give us the averaged description of the system dynamics. Another approaches known as quantum-jump, Monte Carlo wave function (MCWF) and quantum-trajectory methods give theoretical description of single experimental realizations in single quantum system (for example a trapped ion, or cavity-radiation-field mode) and can give one a new insight into physics of processes in the system. Moreover MCWF method gives one possibility to numerically simulate ab initio many processes in complicated quantum systems, taking into account interaction with reservoir (quantum noise), quantized light and other systems of interest.

In this work we investigate the propagation of squeezed coherent field inside a medium of three-level atoms in Electromagnetically Induced Transparency conditions by Monte Carlo wave-function (MCWF) method. Interaction of light with atoms and measurement of parameters of outgoing light are simulated by the method. This allows us to analyze time dynamics of the system "field + atom" and to study the impact of relaxation processes on the system. A part of our numerical results was applied to calculate atomic spin fluctuations spectra and outgoing field squeezing spectra. We find a good correspondence with a theoretical research, carried out by us with the use of Heisenberg-Langevin method, which permits calculation of spectral parameters. In a special case of squeezed vacuum we find a good correspondence with experimental and theoretical results.

The software to conduct numerical simulations was designed taking into account all features of MCWF method, so it can be used for very wide class of problems. It has a modular construction, intuitive graphical interface, which allows a researcher to add new tasks and methods of calculation. In addition our main work the software was tested on such studied problems of quantum optics like the dynamics of laser driven two-level, three-level atom dumped by a zero-temperature quantized radiation field. Spectrum of resonance fluorescence of laser-driven two-level atom, such effects as coherent population trapping and electromagnetically induced transparency in three-level atom were obtained in appropriate conditions.

The research was partially supported by CRDF grant RUP2-2844-NN-06 and RFBR grant 06-02-16739.

Main Topic: T4 Quantum Monte Carlo

Resonating Valence Bond wave function with molecular orbitals: application to dimers.

S. Azadi [1], *M. Casula* [2], *M. Marchi* [1,3], *S. Sorella* [1,3]

1. SISSA, International School for Advanced Studies, 34014, Trieste, Italy.
2. Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau, France.
3. DEMOCRITOS, National Simulation Center, 34014, Trieste, Italy.

We introduce a method for accurate quantum chemical calculations based on a single determinant wave function, the AGP, and a real space correlation factor (the Jastrow factor), that can be efficiently sampled by means of standard quantum Monte Carlo techniques. This allows to obtain a very accurate description of the chemical bond even in extremely difficult cases (such as Be_2, N_2 and C_2) where strong dynamical correlations and/or weak van der Waals interactions are present. The method is based on a constrained variational optimization, obtained with an appropriate number n of molecular orbitals in the AGP wavefunction. It is shown that the most relevant dynamical correlations are correctly reproduced, once n is univocally determined by the requirement to have size consistent results upon atomization to correlated (with Jastrow) Hartree-Fock Slater determinants. Results on test-case dimers are provided.

Main Topic: T4 Quantum Monte Carlo

Equation of state of hexagonal closed packed iron under Earth's core conditions from quantum Monte Carlo calculations

E. Sola[1,2], *J. P. Brodholt*[1,2], *D. Alfè*[1,2,3,4]

1. Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom
2. Materials Simulation Laboratory, University College London, Gower Street, London WC1E 6 BT, United Kingdom
3. Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
4. London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London WC1H 0AH, United Kingdom

We applied quantum Monte Carlo techniques to compute the equation of state of hexagonal closed packed iron in the range of pressure relevant to the Earth's core. We used an accurate iron pseudopotential with a frozen Ne core. Trial wavefunctions have been obtained from density functional theory plane wave calculations, and expanded in systematically improvable B-splines. Tests with various exchange-correlation functionals showed that the B3LYP functional is the one which provided the best trial wavefunctions. DMC calculations were carried out using simulation cells with up to 150 atoms, and corrected for finite size errors using the scheme of Chiesa *et al.* [1] and Kwee *et al.* [2]. The calculated equation of state agrees closely with the experiments [3]. It also agrees with the DFT data [4] and, therefore, reinforces those previous calculations.

[1] S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006)
[2] H. Kwee *et al.*, Phys. Rev. Lett. **100**, 126404 (2008)
[3] K. Mao *et al.*, J. Geophys. Res. **95**, 21737 (1990)
[4] A. Dewaele *et al.*, Phys. Rev. Lett. **97**, 215504 (2006)
[5] P. Söderlind *et al.*, Phys. Rev. B **53**, 14063 (1996)
[6] D. Alfè *et al.*, Phys. Rev. B **61**, 132 (2000)

Main Topic: T5 Ab-initio Molecular Dynamics

Nanoparticle sensitized photorefractive polymers: Modeling the nanoparticles

F. Aslam[1], C.von Ferber[2],

1. Department of Mathematics, Statistics and Engineering Sciences
2. Applied Mathematics Research Centre
Coventry University, Coventry CV1 5FB, United Kingdom

Semiconductor nanoparticles have numerous potential applications[1] because their optical and electronic properties can be readily tuned by varying their size, shape, structure and composition. They are intermediate between bulk and molecular materials, maintaining the crystalline structure of the bulk but with a discrete atom-like energy level structure. The range of optoelectronic applications that can utilise nanoparticles include photovoltaic power production, photorefractive optical data storage[2,3] and processing, as well as nanoscale electronics. Rational engineering of optoelectronic devices is enabled by nanoparticles that are of high quality i.e. are highly mono-disperse and trap-free.

We systematically investigate the electrostatic and structural trends of CdSe nanoparticles using empirical potentials. The stability of the wurtzite structure of the nanoparticle is studied as function of size and shape of the particles. We find significant differences between the properties of approximately spherically shaped particles, and particles with well defined crystal surfaces along different planes as well as nano-rods. For a large part these differences may be related to the strongly varying number of surface dangling bonds within this set of particle shapes. Furthermore, also the aspect ratio of the particle can be shown to have a significant impact on energy, dipole moment and intra-particle pressure. Structural variation with temperature appears to have much less influence.

[1] A.P.Alivisatos, Science, 271, 933 (1996)
[2] F. Aslam , D.J.Binks , M.D.Rahn, D.P.West, P.O'Brien , N.Pickett and S.Daniels , J.Chem. Phys,122 , 184713 (2005)
[3] F. Aslam, D.M.Graham, D.J.Binks , P.Dawson , N.Pickett and P.O'Brien, J. Appl. Phys., 103 ,093702 (2008)

Applications:
A1 Nanoscience
A10 Materials Design

P 0037

Main Topic: T5 *Ab-initio* Molecular Dynamics,

Ab-initio Calculation of High Pressure Phases in InP and InAs Crystals

S. K. Gupta, P. K. Jha, D. Kirin[*] *and I. Luka□evic*[#]
Department of Physics, Bhavnagar University, Bhavnagar, 364022 Gujarat, India
[*]Rudjer Bo□kovi□ Institute, P. O. B. 180, 10002 Zagreb, Croatia
[#]Department of Physics, University J. J. Strossmayer, 31000 Osijek, Croatia

Email: skgupta.physics@gmail.com

Abstract

The sequence of high pressure phases in two III-V semiconducting compound InP and InAs is reported by density functional theoretical calculations. The transition from zero pressure zinc blend phase to its high pressure NaCl phase is the first order and transitions pressures for crystals are in agreement with experiments. The high pressure phase transition from cubic NaCl phase to orthorhombic Cmcm phase in InP and InAs is studied by monitoring the pressure dependence of TA phonon frequencies. The lattice dynamics calculations reveal that the rocksalt structure is unstable with respect to transversal acoustic mode at the Brillouin zone boundary.

Main Topic: T5 Ab-initio Molecular Dynamics

Polymeric Phases of Carbon Dioxide Under High Pressure

Jian Sun[1,6], *Dennis D. Klug*[1], *Roman Marto□ák*[2,3], *Javier Antonio Montoya*[3,5], *Mal-Soon Lee*[4], *Sandro Scandolo*[4,5] *and Erio Tosatti*[3,4,5]

[1] Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Canada
[2] Department of Experimental Physics, Comenius University, 842 48 Bratislava, Slovakia
[3] International School for Advanced Studies (SISSA/ISAS), Trieste, Italy
[4] The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy
[5] INFM-CNR "Democritos" National Simulation Center, Trieste, Italy
[6] Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

The structural transformations of solid carbon dioxide from a molecular solid to a 3-dimesional network solid have challenged researchers for several decades. Here, we employ the recently developed metadynamics method combined with ab initio calculations to provide fundamental insight into recent experimental reports (Refs 1 - 3) on carbon dioxide in the 60 - 80 GPa pressure region. New pressure-induced polymeric phases and their transformation mechanisms are found. Metadynamics simulations starting from the CO2-II ($P4_2/mnm$) at 60 GPa and 600 K proceed via an partially polymerized intermediate, and finally yield a fully tetrahedral, layered structure (P-4m2). Based on the agreement between calculated and experimental Raman and X-ray spectra, it is indicated that the recently identified phase VI [1], assumed to be disordered stishovite-like, is instead the result of an incomplete transformation of the molecular phase into a final layered structure. In addition, a new α-cristobalite-like structure ($P4_12_12$), is predicted to be formed from CO2-III (Cmca) via an intermediate Pbca structure at 80 GPa at low temperatures (< 300 K). Defects in the crystals are frequently observed at 300 K whereas at 500 to 700 K, CO2-III transforms to an amorphous structure, as reported in recent experimental studies[2,3].

Reference:

1. Iota V. et al. Six-fold coordinated carbon dioxide VI. Nature Mat., 6, 34–38 (2007).
2. Santoro, M. et al. Amorphous silica-like carbon dioxide. Nature 441, 857–860 (2006).
3. Kume T. Ohya Y. Nagata M. Sasaki S. and Shimizu H., A transformation of carbon dioxide to nonmolecular solid at room temperature and high pressure. J. Appl. Phys. 102, 053501-053505 (2007).

Main Topic: T6 Large Scale and Multiscale Simulations

Accelerating convergence of large DFT calculations by auxiliary density functionals

Phil Hasnip
University of York (UK)

We present a stable method for accelerating large DFT calculations by replacing conventional charge density mixing algorithms with a parameter-free auxiliary density functional scheme. A model density functional is updated at each self-consistent step, and solved implicitly for the charge density response. This approach suppresses the charge sloshing common in large metallic and inhomogenous systems and can improve convergence substantially.

Main Topic: T6 Large Scale and Multiscale Simulations

Linear-Scaling Density Functional Theory with Tens of Thousands of Atoms: ONETEP

Nicholas D.M. Hine[1], *Peter D. Haynes*[1]

1. Department of Physics and Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

We present recent improvements to the ONETEP code. ONETEP is an ab initio electronic structure package for total energy calculations within density-functional theory. Its main distinguishing features are true 'linear scaling', in that the total computational effort scales only linearly with system size, and 'plane-wave' accuracy, in that the convergence of the total energy is systematically improvable with increasing cutoffs. We present recent improvements to the parallel performance of the code, and thus in effect considerable increases in the scope and scale of feasible calculations with ONETEP, especially in solids. On parallel computers comprising large clusters of commodity servers, our recent improvements make calculations of tens of thousands of atoms in a solid feasible even for small numbers of cores ($10 - 100$). Efficient scaling with number of atoms is demonstrated up to 32,768 atoms on 64 cores, and efficient scaling with number of cores is demonstrated up to 512 cores for 32,768 atoms.

Main Topic: T6 Large Scale and Multiscale Simulations

Multiscale studies on polymeric nitrogen under pressure

Jani Kotakoski, *Karsten Albe*

Materialwissenschaft, Technische Universität Darmstadt, Germany

Existence of polymeric nitrogen was proposed in 1992 by Mailhiot and co-workers [Phys. Rev. B 46, 14419]. Despite significant effort, the structure - labeled as cubic gauche - was synthesized first time a decade later in 2004 by Eremets et al. [Nature Mater. 3, 558]. Interest in this material is due to its enormous energy capacity (more than 140 kJ/mol or 2.0 MJ/g) - 500 times higher than for TNT, for example. This gives promise for applications such as environmentally safe rocket fuel. The material is obtained by applying high pressure and temperature on the conventional molecular nitrogen. Under high pressure, it becomes thermodynamically favored to break the triple bonds between the two atoms in a dimer, and rather form three single bonds with the neighboring atoms.

Even though the cubic gauche structure is considered as a school book example of the predictive power of ab initio calculations, it's far from the complete answer for high pressure phases for nitrogen. In fact, within the last few years, more than twenty different new structures have been proposed.

We use density functional theory to obtain the free energy of different phases at large temperature and pressure ranges (energy minimization and phonon density of states calculations). An extensive 0K comparison of the relevant phases is presented, and extended to higher temperatures for the most stable structures to compare directly the Gibbs free energies. Also presented are the thermodynamically most stable (and dynamically stable) phases at intermediate (188-320 GPa) and high pressures (>320 GPa) which we found recently with our collaborators. Further, we have developed an analytic bond order potential (and extended it to non-bond interactions) in order to mimic the experimental setup. This allows us to follow the phase transitions at atomic scale as well as to optimize the conditions for growing single-crystalline polymeric nitrogen structures. We can also use this method for studying the properties of the amorphous phase often seen in experiments.

P 0042

Main Topic: T6 Large Scale and Multiscale Simulations

Efficiency improvement of localized basis set *ab initio* codes for metallic systems simulations

E. Machado-Charry[1], *J. Iñiguez*[2] *and C.C. Fu*[1]

1. - SRMP-CEA, 91191 Gif-sur-yvette, France
2. ICMAB-CSIC, Campus UAB, 08193 Bellaterra,

The use of Density Functional Theory (DFT) codes based on strictly localized basis set allows accurate electronic structure studies of intermediate and large systems. Among these, SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [1, 2] appears to be one of the most efficient code both in time efficiency and in precision. This is mainly due to the use of a linear combination of numerical pseudo-atomic orbitals as basis set.

Although SIESTA code was initially designed for large non-metallic systems in which only □-point is needed for Brillouin zone (BZ) sampling, it also allows to perform calculations with large ***k*** point-grids, which is essential for an adequate description of relevant properties of metal systems, e.g. the Fermi surface. However, there is an important drawback in SIESTA which penalizes the performance of such calculations. The set of ***k*** points in the BZ, generated from Monkhorst-Pack scheme, does not include only the irreducible set of ***k*** points. In other words, there are subsets of ***k*** points related to each other through symmetry operations. As a consequence, the diagonalization of the Hamiltonian is done several times in a redundant way.

Although the use of an irreducible number of ***k***-points is widely implemented in plane- wave codes, it is not the case for localized-basis codes. In this work, besides of the inclusion of widely used routines for lattice symmetry identification, we show that the method developed here to determine the correct electronic charge density of the system is a specificity of localized-basis DFT codes. The introduction of such methods in SIESTA allows achieving the same level of calculation precision as before, but with significant reduction of CPU time. To highlight this, we will present results on large systems of our interest, i.e. the calculations of defect properties in magnetic transition metals.

References:

1. http://www.uam.es/departamentos/ciencias/fismateriac/siesta/
2. José M. Soler, Emilio Artacho, Julian D. Gale, Alberto García, Javier Junquera, Pablo Ordejón and Daniel Sánchez-Portal *J. Phys.: Condens. Matter* **14**, 2745 (2002)

Main Topic: T6 Large Scale and Multiscale Simulations

Large-scale DFT calculations on DNA systems with the order-N DFT program CONQUEST

T. Otsuka[1], *T. Miyazaki*[1], *T. Ohno*[1], *D. R. Bowler*[2], *M. J. Gillan*[2]

1. Computational Materials Science Center, National Institute for Materials Science, Tsukuba, Ibaraki, Japan
2. Department of Physics and Astronomy, University College London, London, United Kingdom

We report our recent progress in applications of the order-N (O(N)) DFT program CONQUEST. The code is efficient on massively parallel computers and has an ability to treat systems containing more than ten thousands of atoms. CONQUEST minimizes DFT total energy with respect to the Kohn-Sham density matrix. Here, we present our recent study on hydrated DNA system. The system consists of 3439 atoms (634 atoms for a DNA of d(CCATTAATGG)$_2$ (PDB code 1WQZ), 9 Mg counter ions and 932 water molecules). We have found that the O(N) DFT calculations using density matrix minimization method are robust and accurate. The dependence of the total energy on the cutoff radius of the (auxiliary) density matrix is shown in figure 1 and we can see that the energy converges very rapidly. We have also compared the atomic forces calculated by CONQUEST with those by AMBER. Figure 2 shows the force components for the atoms of Ade3 part, which includes the atom having the largest force components. We find that these two methods show qualitative or even semi quantitative agreements for these atoms. Detailed analysis will be reported.

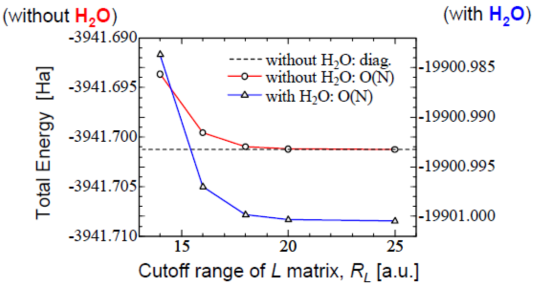


Figure 1. Dependence of total energy on cutoff length R_L of the auxiliary density matrix in O(N) calculations.

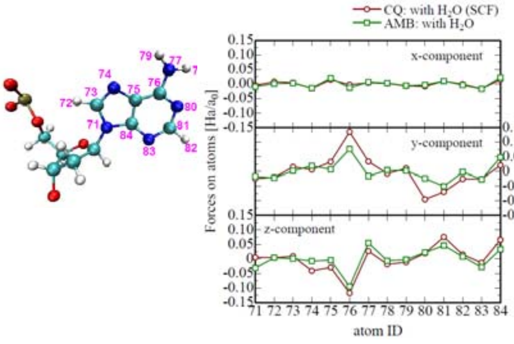


Figure 2. Atomic force components calculated by CONQUEST and AMBER for the atoms of Ade3 part.

References

[1] D. R. Bowler, R. Choudhury, M. J. Gillan, T. Miyazaki, phys. stat. sol. (b) **243**, 989 (2006). [2] M. J. Gillan, D. R. Bowler, A. S. Torralba, T. Miyazaki, Comp. Phys. Comm. **177**, 14 (2007). [3] T. Otsuka, T. Miyazaki, T. Ohno, D. R. Bowler, M. J. Gillan, J. Phys. Condens. Matter **20**, 29401 (2008).

Main Topic: T6 Large Scale and Multiscale Simulations

A Maximally-Localised Wannier Function Approach to Superlatticed Si/Ge Nanowires

Matt Shelley[1], *Arash Mostofi*[1]

1. The Thomas Young Centre, Imperial College, London

A study of superlatticed Si/Ge nanowires for thermoelectric applications is presented, which uses a maximally-localised Wannier function (MLWF) basis to construct large period superlattices from smaller fragments. Density-functional theory in the pseudopotential plane-wave approximation is used to determine the structures and ground-state electron density of hydrogen-passivated Si and Ge nanowires. Similar calculations are made on a supercell containing a sharp Si/Ge interface. We convert the Bloch eigenstates of the three fragments to a MLWF basis. Using Hamiltonians in this localised basis we aim to construct model Hamiltonians of large period superlatticed nanowires. Bandstructures, local density of states and the quantum conductance of test cases are included to discuss details of the method.

Main Topic: T7 Activated Processes

Palladium impurities in cubic silicon carbide: steps towards the nucleation of a silicide

Guido Roma[1]

1. Service de Recherches de Métallurgie Physique, CEA-Saclay, France

Silicon carbide has been used in nuclear industry and is still considered as a coating material for nuclear fuel. Its main role should be to retain fission products. It has been observed, however, that some fission products, in particular palladium, attack the SiC layer and are supposed to be responsible for corrosion of the material, which ultimately leads to failure of the cladding and to the release of fission products. I used first principles calculations based on Density Functional Theory (DFT) in order to investigate the energetic, structural, and kinetic properties of Pd impurities inside β-SiC; in particular I investigated substitutional and interstitial insertion sites in several charge states, with a special care to assess the convergence of solution energy with the size of the supercell for neutral and charged species. The results show that substitutional impurities are expected to be dominant, however their solution energy, higher than 3 eV, indicates a strong driving force towards the formation of Pd_2Si. In order to understand the very early stages of the nucleation process one needs a lot of informations on migration barriers and the stability of small clusters. Substitutional impurities are expected to have low mobility, due to the high migration barrier of vacancies; interstitial impurities are more mobile. I present the results for migration barriers of interstitial impurities, including some effect of the charge state, and a barrier for the clustering of two Pd atoms. Some configurations for di-Pd and tri-Pd clusters will be shown. The energy barriers were calculated either with the Nudged-Elastic-Band (NEB) method or through constrained relaxations. I will discuss the role of electron and carbon/silicon chemical potential conditions on the corrosion process.

Main Topic: T8 Electronic and Thermal Transport

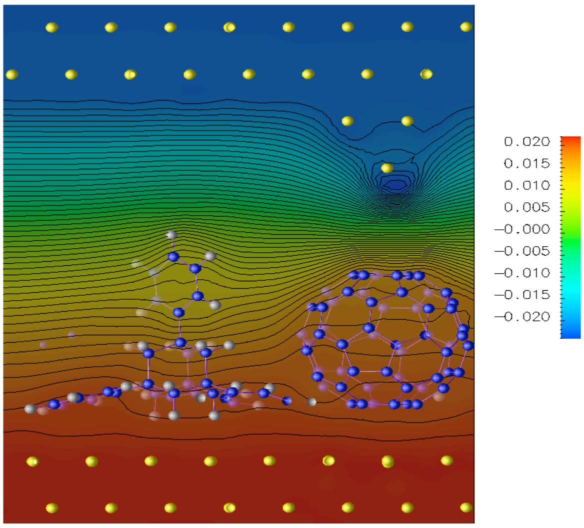
Electron transport simulations through C_{60}-based nanostructures on Au(111)

M. Cobian[1],F.D. Novaes[1], H. Ueba[2], A. Garcia[1], P. Ordejon[3], N. Lorente[3]

1. ICMAB-CSIC, Campus de la UAB, 08193 Bellaterra, Spain
2. Department of Electronics, Toyama University, Gofuku, Toyama 930-855, Japan
3. CIN2, Campus de la UAB, 08193 Bellaterra, Spain

Molecular entities at the interface with an inorganic surface are the basis for new hybrid functional materials for microelectronics.
In most cases, strong bonding of molecules to metal surfaces perturbs the discrete molecular energy levels leading to a broadening of the molecular density of states. Deposition of C_{60} on a Au(111) surface previosly exposed to tetraphenyl adamantane give rises to a nanostructured organic layer where the electronic coupling between the C_{60} and the Au(111) surface is significantly reduced compared to C_{60} on a clean Au(111) surface [1].
In this case molecular states of C_{60} remain more localized and less broadened, thus giving rise to strong non-linearities in the electron transport through the organic-inorganic interface. Calculations based on Density Functional Theory reveal that intermolecular interactions lock C_{60} into a particular orientation.
Scanning tunneling spectroscopy experiments on such system exhibit the presence of negative differential resistance that motivated the simulation of the transport properties at ab-initio level using TRANSIESTA.

[1] KJ. Franke, G. Schulze, N. Henningsen, I. Fernandez-Torrente, JI. Pascual, S. Zrwell, K. Ruck-Braun, M. Cobian, N. Lorente *Physical Review Letters* **2008**, *100*, 036807



Voltage drop through the organic layer

Main Topic: T8 Electronic and Thermal Transport

Charge transport in a single-helix of the T3-785 peptide: *ab initio* dipeptide structures, ionization energies, and hopping integrals

L. Leite[1], *V. N. Freire*[1], *N. Saker Neto*[2], *B. S. Cavada*[2], *E. W. S. Caetano*[3], *E. L. Albuquerque*[4], *M. S. de Vasconcelos*[5]

1. Departamento de Física, Universidade Federal do Ceará,
Caixa Postal 6030, 60455-900 Fortaleza, Ceará, Brazil
2. Departamento de Bioquímica, Laboratório de Bioquímica Molecular,
Universidade Federal do Ceará, Campus do Pici, 60455-900 Fortaleza, Ceará, Brazil
3. Centro Federal de Educação Tecnológica do Ceará,
Av. 13 de Maio, 2081, Benfica, 60040-531 Fortaleza, Ceará, Brazil
4. Departamento de Física Teórica e Experimental,
Universidade Federal do Rio Grande do Norte, 59072-970 Natal, Rio Grande do Norte, Brazil
5. Centro Federal de Educação Tecnológica do Marenhão
Av. Getulio Vargas, 04, Monte Castelo 65030-000 São Luís, Maranhão, Brazil

Research on charge transport in proteins was pioneered by Szwenty-GyÄorgyi in 1941 [1, 2], who reported a semiconductor character instead of insulator. However, from early measurements it was not clear whether the conductivity originated from the proteins or from impurities in the samples. The initial theoretical investigations on charge transport in periodic polypeptides focused band structures determined by semi-empirical an *ab initio* methods. First was suggested that conductivity in proteins was caused by the delocalization of the electrons, but later the possibility of hopping conductivity was considered. Ladik and co-workers [3] developed at the *ab initio* level a theory of hopping conductivity in pig insulin, one of the smallest native protein hormones, obtaining formulas for the determination of primary hopping frequencies. Their results confirmed that the AC conductivity of a native protein could be caused by hopping of the charge carriers between different localized centers of orbitals. Stimulated by these works, a tight binding charge transport modeling of a single helix T3-785 peptide based on the 12- residue amino acid sequence 785-796 of human type III collagen is performed in this work, considering its primary sequence. The amino acid vertical ionization energies and hopping integrals for isolated dipeptides of the T3-785 primary sequence are obtained by *ab initio* calculations within the generalized gradient approximation (GGA). The density of states and charge transmission through T3-785 is obtained using this data, pointing to this strategy as a viable one to obtain an estimate of the T3-785 charge transport characteristics. The hopping integrals for isolated dipeptides are demonstrated to be similar to those calculated considering the T3-785 secondary structure. This result suggests the usefulness of constructing a library of *ab initio* calculated hopping integrals for isolated dipeptides to be used for a first evaluation of charge transport in any protein.

[1] A. Szent-Gyrgyi, Nature 148, 157 (1941).
[2] A. Szent-Gyrgyi, Science 93, 609 (1941).
[3] Y.-J. Ye, J. Ladik, Phys. Rev. B48, 5120 (1993).

Main Topic: T8 Electronic and Thermal Transport

Toward numerically accurate first-principles calculations of nano-device charge transport properties: Applications to alkane and polyene junctions

Yong-Hoon Kim [1]

1. Department of Materials Sciences and Engineering, University of Seoul, Seoul, 130-743 Korea

After briefly describing a first-principles computational package we have developed [1,2], we report its application to the coherent charge transport properties of single *N*-alkane and *N*-polyene molecules (N = 6, 8, 10, and 12) thiolate-bridged to flat Au(111) electrodes. For the alkane junctions, the conductance scaling data are compared with those from recent experiments and other calculations. For the polyene junctions, we find a surprising metallic behavior [1]. We describe several measures that resolve the so-called band lineup problem in the charge transport calculations and explicitly demonstrate the errors arising from including an insufficient number of electrode metal atoms within the scattering region [3,4]. We also describe the improvements made in our program that enable us to treat larger systems more efficiently and accurately [4].

Acknowledgments: This work was supported by the Korea Science and Engineering Foundation (grant no. 2008-02807) and the Korea Research Foundation (grant No. KRF-2007-331-C00077).

References:

[1] Y.-H. Kim, J. Tahir-Kheli, P. A. Schultz, and W. A. Goddard III, *"First-principles approach for the charge transport characteristics of monolayer molecular electronic devices: Application to hexanedithiolate devices"*, Phys. Rev. B **73**, 235419 (2006)
[2] Y.-H. Kim, *" "Toward numerically accurate first-principles calculations of nano-device charge transport properties: The case of alkane single-molecule junctions""*, J. Kor. Phys. Soc. **52**, 1181~1186 (2008).
[3] C. George, H. Yoshida, W. A. Goddard III, S. S. Jang, and Y.-H. Kim, *"Charge transport through alkane and alkene self-assembled-monolayers from multiscale computer simulations"*, J. Phys. Chem. B (to be published)
[4] Y.-H. Kim, *"Electrical and mechanical switching in a realistic [2]rotaxane device model"*, J. Nanosci. Nanotech. **8**, 4593-4597 (2008).

Charge transport in chemically doped 2D graphene

Aurélien Lherbier[1], *Xavier Blase*[2], *Yann-Michel Niquet*[3], *François Triozon*[4], *Stephan Roche*[5]

1. Unité de Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium
2. Institut Néel, CNRS and Université Joseph Fourier, B.P. 166, 38042 Grenoble cedex 09, France
3. CEA, Institute for Nanosciences and Cryogenics (INAC), SP2M/L Sim, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
4. CEA, LETI-Minatec, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
5. CEA, Institute for Nanosciences and Cryogenics (INAC), SPSMS/GT, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Graphene, as carbon nanotubes[1], is an attractive material which has a rather unique electronic structure with linear dispersion near the charge neutrality point[2]. Its good transport properties and its practical aspects for design of electronic devices could make the graphene the next material of choice in nanoelectronic. Investigation of the robustness of its good transport properties in the presence of disorder, like edge roughness or impurities, is a key issue[3].

We report here on a numerical study of electronic transport in chemically doped 2D graphene materials[4]. By using ab initio calculations, a self-consistent scattering potential is derived for boron and nitrogen substitutions, and a fully quantum-mechanical Kubo-Greenwood approach is used to evaluate the resulting charge mobilities and conductivities of systems with impurity concentration ranging within [0.5, 4.0]%. Even for a doping concentration as large as 4.0%, the conduction is marginally affected by quantum interference effects, preserving therefore remarkable transport properties, even down to the zero temperature limit. As a result of the chemical doping, electron-hole mobilities and conductivities are shown to become asymmetric with respect to the Dirac point.

References

[1] J. C. Charlier, X. Blase and S. Roche, Rev. Mod. Phys. **79**, 677 (2007)

[2] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, arXiv **0709.1163**, (2008), accepted for publication in Review of Modern Phys. (2008)

[3] A. Lherbier, B. Biel, Y. M. Niquet and S. Roche, Phys. Rev. Lett. **100**, 036803 (2008)

[4] A. Lherbier, X. Blase, Y. M. Niquet, F. Triozon and S. Roche, Phys. Rev. Lett. **101**, 036808 (2008)

T8

Vibrational Properties of TiO_2

E. Shojaee and M.R. Mohammadizadeh

Superconductivity Research Laboratory(SRL), Department of Physics, University of Tehran, Tehran, Iran

Abstract

Dynamical properties of Anatase were studied in the framework of density functional perturbative theory (DFPT). The Born effective charges, Dielectric tensor, phonon band structure and density of states were in local density approximation (LDA) and generalized gradient approximation (GGA) reported, too. Using the phonon band structure, the elastic constants of Anatase were calculated by linear fit to the acoustical branches near the zone center in symmetry directions of the crystal. It was observed that the elastic constants which was obtained in GGA were in more agreement with those calculated by the stress-strain relation, can this also be improved with more energy cutoff in wave functions. This approach leads us to know the accuracy of the calculated acoustic branches in phonon band structure which is the most challenging part of the band structure. So, the phonon band structure becomes quantitative and is useful to obtain the most important mechanical properties of the materials. In addition it was observed that if LDA is successful in calculation the zone-center modes, GGA is more to obtain the descents of acoustic branches.

Main Topic: T8 Electronic and Thermal Transport, A10 Materials Design

First Principle Calculation of Tunneling Current through SiO_2 and SiO_xN_y Gate Dielectrics in MOSFETs

E. Nadimi[1], *P. Plänitz*[1,3], *R. Öttking*[3] *and C. Radehaus*[2,3]

[1] Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany
[2] Fakultät für Elektrotechnik und Informationstechnik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany
[3] GWT-TUD GmbH - Geschäftsstelle Chemnitz, Annaberger Str. 240, 09125 Chemnitz, Germany

Improving the performance of metal-oxide-semiconductor field effect transistor (MOSFET) devices in terms of higher degree of integration and faster devices has required larger gate capacitance in each new technology generation. To date, this has been achieved mainly by decreasing the gate oxide thickness, which has reached values as small as 1.5 nm. Calculation of gate tunneling current through such thin gate oxide, as a major design consideration, is of great importance. To date, most of the calculations through SiO2 or other gate dielectric stacks are based on the effective mass approximation; either assuming a single parabolic dispersion with an energy-independent tunneling effective mass or a Franz-type energy-dependent one. But, it is unclear how to associate an effective mass to electrons in a stacked gate dielectric with complex interfacial layer and profile of transition metals or nitrogen. Indeed, in ultra-thin gate dielectrics the effective mass approximation fails and an atomic scale approach is necessary. Furthermore, applying such atomic scale approach provides a method to investigate atomic bonding, dislocations and vacancies, as well as their influence on the tunneling current.

In the following work, a combination of density functional theory (DFT) and ballistic transport theory within the non-equilibrium Green's function formalism is applied to the calculation of $Si/SiO_2/Si$ and $Si/SiO_xN_y/Si$ model interfaces and the tunneling current through these structures. The interface structure of Si/SiO_2 is constructed based on β-cristobalite SiO_2, which shows the lowest mismatch on the Si (100) surface. The oxynitride interfaces are constructed based on local bonding of N atoms in bulk oxynitride and in the way that the structures remain dangling-bond free. For the calculation of tunneling current the structures are sandwiched between two highly doped Si electrodes at different potentials.

Two identical SiO_2 gate dielectric with different thickness as well as two oxynitride gate dielectrics with different thickness and nitrogen concentration are considered in our study. Comparing two SiO_2 gate dielectrics shows that the band edges are almost unchanged but the transmission probability is much lower in the thick sample. The result of this lower transmission probability is a lower tunneling current in the thick sample. On the other hand, doping SiO_2 with N atoms results in a lowering of the band gap. As the N concentration increases the density of states within the band gap of SiO_2 rises and lead to higher leakage currents. Like as semi-classical models our calculation predicts a higher slope of I-V curves for gate dielectrics with lower band gap such as oxynitride.

Main Topic: T8 Electronic and Thermal Transport

Tunneling across a ferroelectric barrier: a first-principles study

Frederico D. Novaes[1], *D. Bilc*[2], *P. Ordejon*[3], *J. Iniguez*[1] *and P. Ghosez*[2]

1. Institut de Ciència de los Materials de Barcelona - CSIC, Spain
2. Physique Théorique des Matériaux, Université de Liège, Belgium
3. Centre d'Investigacio en Nanociència i Nanotecnologia - CSIC, Spain

Ferroelectric tunnel junctions (FTJ), including a ferroelectric as the barrier material, have recently attracted a lot of interest since they are potentially interesting for technological applications such as data storage. In such system, the barrier has to be sufficiently thin to allow for tunneling but must at the same time remain ferroelectric, a property that tends to be suppressed in ultrathin films. Up to now, the modeling of FTJ has remained at the semi-empirical level. Here, we consider a prototypical system made of a ferroelectric oxide film between two gold electrodes and compute the I-V curve of the system using density functional theory and Non-Equilibrium Green's Function (NEGF+DFT) formalism. Our atomic-scale approach allows for the first time accurate and self-consistent description of the screening at the metal ferroelectric interface and of the atomic relaxation. It predicts that the asymmetry in the I-V curve for up and down polarizations is sufficiently large to be detected experimentally, therefore opening the door to applications in which the tunneling current allows the reading of the polarization state. Work supported by FAME-EMMI.

Main Topic: T8 Electronic and Thermal Transport

First-Principles Calculation for Leakage Current through Si/SiO$_2$ Interface

Tomoya Ono
Graduate School of Engineering, Osaka University, Japan

Controlling the structure of the Si/SiO$_2$ interface on the atomic scale is the most intensively studied topic for silicon device scaling. The defects at Si/SiO$_2$ interfaces cause serious problems such as the increased gate leakage current, the reduced threshold for dielectric breakdown, and oxide charging[1,2]. These problems are known to degrade the dielectric reliability and the device performance. The ideal stacking structure of Si/ SiO$_2$ is the interface consisting of only silicon and oxygen atoms without any defects. Annealing of SiO$_2$ films in hydrogen ambient, in which the dangling bonds are terminated by the hydrogen atoms, is also a successful method to reduce defects in SiO$_2$ films and at the interface, and has been used as a standard technique in the semiconductor industry. The degradation of devices has been attributed to hydrogen releasing from dangling bonds by hot electrons and diffusing to the interface. When the SiO$_2$ layer becomes very thin (ca 15 Å), these defects are expected to increase drastically the leakage current through such thin films as well as change the dielectric properties of interfaces. I present a first-principles study on electron-conduction properties of thin silicon oxide films using the first-principles calculation code for electronic structures and electron-conduction properties of nanostructures[3].

I found that the dangling bonds aligned parallel to the interface do not affect the leakage current significantly. On the other hand, the dangling bonds aligned perpendicular to the interface results in the largest leakage current, and therefore, it causes dielectric breakdown. In addition, the hydrogen termination of the dangling bonds significantly reduces decrease the leakage current.

1. S.M. Sze, Physics of Semiconductor Devices, (Wiley-Interscience , New York, 1981).
2. S. Takagi, A. Toriumi, M. Iwase and H. Tango, IEEE Transactions on Electron Devices, 41, 2357, (1994) references therein.
3. K. Hirose, T. Ono, Y. Fujimoto, and S. Tsukamoto, *First-Principles Calculations in Real-Space Formalism, Electronic Configurations and Transport Properties of Nanostructures* (Imperial College Press, London, 2005).

Main Topic: T8 Electronic and Thermal Transport

Electron-phonon scattering in semiconducting nanostructures: *ab initio* approach.

Jelena Sjakste[1], *Nathalie Vast*[1], *Valeriy Tyuterev*[1,2]

1. Ecole Polytechnique, Laboratoire des Solides Irradiés, CEA-DSM-DRECAM, CNRS, 91128 Palaiseau, France.
2. Tomsk State Pedagigical University, Tomsk, Russia.

The interaction of excited electrons with phonons plays a central role for electronic and transport properties at the nanoscale. It is the dominant process limiting the excitation lifetime at medium excitation energies. Despite its importance, a reliable *ab initio* approach to describe the electron-phonon interaction in nanostructures is still lacking. The theoretical models used in the past, which are often oversimplified, need revisiting and justification.

Recently, we developed a fully *ab initio* approach to calculate the electron-phonon constants and scattering times for collisions of carriers in the conduction band with short-wavelength phonons [1,2]. We applied it to the deexcitation of hot electrons in GaAs [1,2], and to the lifetime of the direct exciton in GaP and GaAs [2,3], all in excellent agreement with experiments. Our next goal is to study the effects of nanostructuring on the electron-phonon coupling constants. We will discuss our first results for the the electron-phonon coupling constants in GaAs/AlAs superlattices.

[1] J. Sjakste, N. Vast, V. Tyuterev, Phys. Rev. Lett. 99, 236405 (2007).
[2] J. Sjakste, V. Tyuterev, N. Vast, Appl. Phys. A 86 (2007) 301.
[3] J. Sjakste, V. Tyuterev, N. Vast, Phys. Rev. B 74, 235216 (2006).

Main Topic: T8 Electronic and Thermal Transport

First-Principles Calculations of the Electrical Conductance and Seebeck Coefficient in Molecular Junctions

C. Tabares-Mendoza[1]*, F. Novaes*[2]*, P. Ordejón*[3]

1, 3. Centro de Investigación en Nanociencia y Nanotecnología – CIN2 (CSIC-ICN),
Campus de la UAB, E-08193, Bellaterra, Barcelona (Spain)
2. Instituto de Ciencia de Materiales de Barcelona (CSIC), Campus UAB, E- 08193,
Bellaterrra, Barcelona (Spain)

The study of charge transport through molecular junctions is usually carried out by measuring its current-voltage characteristics. However, it has been proposed on the basis of theory [1] that the measurement of the Seebeck coefficient (*S)* could provide important information not accessible to standard conductance measurements. In particular, the thermoelectric voltage provides information on the Fermi level's location relative to the molecular orbitals. A recent experimental report [2] has demonstrated the feasibility to use the Seebeck coefficient to determine experimentally the character of the carriers in molecular junctions. The measurements also find a linear dependence of *S* with molecular length for a series of organic molecules.

In this work we have performed transmission calculations for the experimental set-up used in [2]: the series of molecules benzene-, dibenzene- and tribenzene-dithiol attached to gold (111) electrodes. The calculations were done from first-principles, using the TranSIESTA [3] scheme, which is based on Density Functional Theory (DFT) and determines the self-consistent electronic structure of a nanostructure coupled to semi-infinite electrodes, via the Non-Equilibrium Green's function (NEGF) formalism.

We find that the Seebeck coefficient obtained in our calculations only differ from the experimental measurements by a small fraction in their values, whereas the conductance differ by more than one order of magnitude between theory and experiments (as is common in these molecular systems). The linear dependence of *S* on the molecular length was also observed and the sign of *S* indicates that the Fermi level is closer to the HOMO orbital, hence a p-type conduction is expected.

We analyse the results in terms of the molecular orbitals participating in the conduction, and propose a model to explain the linear dependence of *S* with the molecular length, and the difference in behaviour of the conductance and thermoelectric power in the comparison between theory and experiments.

References
(1) M. Paulsson, S. Datta *Physical Review B* **2003**, *67*, 241403(R)
(2) P. Reddy, S.-Y., Jang, R. A. Segalman, A. Majumdar *Science* **2007**, *315*, 1568
(3) M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, K. Stokbro,
Physical Review **2002***, 65*, 165401

Main Topic: T8 Electronic and Thermal Transport

Boosting metallic nanotube interconnects: increasing current at high field with isotopic disorder

Vandecasteele Niels[1], *Lazzeri Michele*[1], *Mauri Francesco*[1]

1. IMPMC, Pierre et Marie Curie University (Paris, France)

Metallic carbon nanotubes can carry the highest current density before they break. This makes them the best candidates as interconnects in future electronic devices. However, for voltages > 0.2 V, the measured IV curve of metallic tubes displays a sudden increase of the resistivity which is due to the scattering with optical phonons. Recently, we have shown [1,2] that the largest part of this electrical resistivity is due to the presence of an anomalously-high optical-phonon occupation (hot phonons). Indeed, during transport, the conducting electrons scatter with optical phonons. If the rate at which optical phonons are generated is faster than the rate at which they can release energy to the system, their population increases. This hot-phonon generation, in turn, augments the electrical resistivity of the system. We will show that it is possible in practice to improve the electrical performances of metallic tubes by ^{13}C isotope enrichment [3]. The mass disorder scatters phonons but not electrons. This results in a reduction of hot phonon population and in a decrease of the nanotube differential resistance at high field by more than a factor of two [3].

[1] Lazzeri, Piscanec, Mauri, Ferrari, Robertson, Phys. Rev. Lett. **95**, 236802 (2005)
[2] Lazzeri, Mauri, Phys. Rev. B **73**, 165419 (2006).
[3] Vandecasteele, Lazzeri, Mauri, to be published

Main Topic: T9 Response to External Fields

New developments in Density Functional Perturbation Theory

Andrea Dal Corso[1,2]

1. SISSA, Via Beirut 2/4, 34014 Trieste (Italy)
2. DEMOCRITOS, Via Beirut 2/4, 34014 Trieste (Italy)

I present two extensions of density functional perturbation theory (DFPT). First, I discuss DFPT for a functional written in terms of spinor wave-functions which can deal with spin-orbit coupling effects via fully relativistic ultrasoft pseudo-potentials, [1] and I apply the theory to the phonon dispersions of fcc-Au, fcc-Pt and fcc-Pb. [2] Then, I discuss DFPT within the projector augmented-wave (PAW) method. With respect to the formulas presented by C. Audouze et al., [3] my expressions require only minor modifications of DFPT written for ultrasoft pseudo-potentials. [4] The method is validated by calculating the frequencies of the vibrational modes of two molecules, CO and H_2O, and the phonon dispersions of C in the diamond structure.

References

[1] A. Dal Corso, Phys. Rev. B **76**, 054308 (2007).
[2] A. Dal Corso, Phys.: Condens. Matter **20**, 445202 (2008).
[3] C. Audouze, F. Jollet, M. Torrent, and X. Gonze, Phys. Rev. B **78**, 035105 (2008).
[4] A. Dal Corso, Phys. Rev. B **64**, 235118 (2001).

Main Topic: T9 Response to External Fields

First-Principles Calculations of Lattice-Mediated Magnetoelectric Effects

Jorge Íñiguez and Jacek C. Wojdeł

Institut de Ciencia de Materials de Barcelona (CSIC), 08193 Bellaterra, Spain

We have developed a microscopic theory of the magnetoelectric response of an insulator, and derived from it an analytical expression for the lattice-mediated part of the effect [1]. Such a result provides us with distinct hints at strategies to increase the magnitude of the response, as well as with a convenient method for performing first-principles calculations. Here we will illustrate the usefulness of the proposed approach with applications to Cr_2O_3, a model magnetoelectric crystal, and $BiFeO_3$ and related compounds, the best studied, and arguably most technologically promising, family of multiferroics.

[1] J. Íñiguez, Phys. Rev. Lett. **101**, 117201 (2008).

Main Topic: T9 Response to External Fields

Nonadiabatic wavepacket dynamics: k-space formulation

Miguel Pruneda[1], Ivo Souza[2]

1. Centre d'Investigacio en Nanociencia i Nanotecnologia, CIN2-CSIC, Barcelona (SPAIN)
2. Department of Physics, UC Berkeley (USA)

The time evolution of wavepackets in crystals in the presence of a homogeneous electric field is formulated in k-space in a numerically tractable form. The dynamics is governed by separate equations for the motion of the waveform in k-space and for the evolution of the underlying Bloch-like states. A one-dimensional tight-binding model is studied numerically, and both Bloch oscillations and Zener tunneling are observed. The long-lived Bloch oscillations of the wavepacket center under weak fields are accompanied by oscillations in its spatial spread. These are analyzed in terms of a k-space expression for the spread having contributions from both the quantum metric and the Berry connection of the Bloch states. We find that when sizeable spread oscillations do occur, they are mostly due to the latter term..

Main Topic: T9 Response to external fields

Theory of orbital magnetoelectric polarizability in insulators

David Vanderbilt[1], Andrew Essin[2], Joel Moore[2,3]

1. Dept. of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854
2. Department of Physics, University of California, Berkeley, CA 94720
3. Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The linear magnetoelectric coupling in a crystalline solid can be expressed as $\alpha_{ij} = \partial^2 E/\partial\mathcal{E}_i \partial B_j = \partial P_i/\partial B_j = \partial M_j/\partial\mathcal{E}_i$, where $\mathcal{E}$ and B are electric fields and E is the energy density. In general α_{ij} has lattice and Zeeman contributions, but we focus here only on the frozen-ion part involving orbital magnetization. We claim[1] that this *orbital magnetoelectric polarizability* (OMP) has a *scalar* form

$$\alpha_{ij}^{\mathrm{OMP}} = \frac{\theta}{2\pi}\frac{e^2}{h}\delta_{ij}$$

and that θ can be computed from the crystalline bandstructure using the formula

$$\theta = \frac{1}{2\pi}\int_{\mathrm{BZ}} d^3k \; \epsilon_{ijk}\,\mathrm{Tr}[\mathcal{A}_i\partial_j\mathcal{A}_k - i\frac{2}{3}\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k]$$

where the integral is over the Brillouin zone, ϵ_{ijk} is the antisymmetric tensor, $\mathcal{A}_j^{\mu\nu}(\mathbf{k}) = i\langle u_{\mathbf{k}\mu}|(\partial/\partial k_j)|u_{\mathbf{k}\nu}\rangle$ is the Berry connection matrix, and Tr is a trace over occupied bands μ. This is essentially Eq. (78) of Ref. [2], although we have derived it[1] based on a theory of the polarization induced by a crystal Hamiltonian having a slow spatial variation.[3] The theory of the OMP θ is strongly analogous to that of the electric polarization P, with θ being related to a second Chern index in the same sense that P is related to a first Chern index. In the presence of time-reversal (or inversion) symmetry, θ must be 0 or π, with $\theta = \pi$ indicating a "strong topological insulator" in the sense of the generalization of 2D Z_2 (quantum spin Hall) insulators to 3D.[4,5] The quantum of indeterminacy of θ can be understood by noting that θ is a measure of the dissipationless surface Hall conductivity σ_{xy}, and the possibility that the crystal surface may behave as a Chern insulator insures that σ_{xy} is only well defined modulo 2π.

---

[1] A.M. Essin, J.E. Moore, and D. Vanderbilt, arXiv:0810.2998.

[2] X. Qi, T.L. Hughes, and S.-C. Zhang, arXiv:0802.3537.

[3] D. Xiao, J. Shi, D.P. Clougherty, and Q. Niu, arXiv:0711.1855.

[4] J.E. Moore and L. Balents, Phys. Rev. B **75**, 121306 (2007).

[5] L. Fu, C.L. Kane, and E.J. Mele, Phys. Rev. Lett. **98**, 106803 (2007).

Main Topic: T9 Response to External Fields

Optical saturation driven by exciton confinement in molecular chains: a TDDFT study.

Daniele Varsano[1,4], *Andrea Marini* [2,4], *Angel Rubio*[3,4]

1. National Center on nanoStructures and Biosystems at Surfaces (S3) of INFM–CNR, Modena, Italy
2. Istituto Nazionale per la Fisica della Materia e Dipartimento di Fisica dell'Universitá di Roma "Tor Vergata", Roma, Italy
3. Nano-Bio Spectroscopy Group and Unidad de Física de Materiales Centro Mixto CSIC-UPV, Universidad del País Vasco UPV/EHU, Donostia, Spain
4. European Theoretical Spectroscopy Facility (ETSF).

We identify excitonic confinement in one–dimensional molecular chains (i.e. polyacetylene and H_2) as the main driving force for the saturation of the chain polarizability as a function of the number of molecular units. This conclusion is based on first principles time–dependent density functional theory calculations using a recently developed exchange–correlation kernel that accounts for excitonic effects. The failure of simple local and semi–local functionals is shown to be linked to the lack of memory effects, spatial ultra–non–locality, and self–interaction corrections. These effects get smaller as the gap reduces, in which case such simple approximations do perform better.

Main Topic: T9 Response to External Fields

Density Functional Perturbation Theory with Spin-Orbit Coupling: Phonon Band Structure of Lead

Matthieu J. Verstraete[1,2,4], *Marc Torrent*[3], *François Jollet*[3],
Gilles Zérah[3], *Xavier Gonze*[1,4]

1. Unité PCPM and CERMIN, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

2. Physics Dept. University of York, Heslington, YO10 5DD, United Kingdom

3. Commissariat à l'énergie atomique, F-91680 Bruyères-le-Châtel, France

4. European Theoretical Spectroscopy Facility (ETSF)

The effect of spin-orbit coupling on phonon band structures can be profound for materials containing heavy elements. We describe our implementation of Density Functional Perturbation Theory with the spin-orbit interaction, for norm-conserving pseudopotentials. We show that the spin-orbit effect on the phonon frequency at the X point in face-centered cubic Pb is very large: it explains the discrepancy between calculated and experimental frequencies previously observed by De Gironcoli [Phys. Rev. B 53, (1996) R7575]. Several technical issues (the exchange-correlation functional, the presence of semicore states, the pseudization scheme, and the real-space range of inter-atomic force constants) are also investigated.

Main Topic: T11 Other Methods (Quantum Molecular Dynamics beyond the Born-Oppenheimer Approximation)

How Good is Damped Molecular Dynamics as a Method for Simulating Radiation Damage in Metals?

J le Page, D R Mason, C P Race, M W Finnis, A P Horsfield, A P Sutton, and W M C Foulkes

Imperial College London

Classical molecular dynamics (MD) is often used to study radiation damage cascades because it provides information on time and length scales inaccessible to experiment. In a radiation damage process, energy transfer from ions to electrons may be important, but there is continued uncertainty over how to incorporate such effects in MD. We introduce a new quantum mechanical simulation technique to evaluate different methods of accounting for electronic losses. The irreversible transfer of energy from fast ions to electrons does not take place in conventional Born-Oppenheimer quantum MD simulations, but can be studied using Ehrenfest-based quantum MD. Our Ehrenfest simulations suggest that a damping force proportional to velocity is sufficient to model energy transfer from ions to electrons in most low energy cascades. We also find, however, that a larger rate of energy transfer is seen when the ionic kinetic energy is confined to a focused sequence of collisions. A viscous damping coefficient dependent on the local atomic environment is shown to be an excellent model for electronic energy losses in low energy cascades in metals.

Main Topic: T11 Other methods

New developments in SIESTA

E. Artacho[1], *E. Anglada*[2], *O. Diéguez*[3], *J.D. Gale*[4], *A. García*[3], *J. Junquera*[5], *P. Ordejón*[6], *J.M. Pruneda*[3], *D. Sánchez-Portal*[7], *J.M. Soler*[2]

1. Dept. of Earth Sciences, Univ. of Cambridge
2. Dept. Física de la Materia Condensada, Univ. Autónoma de Madrid, Spain
3. Inst. de Ciencia de Materials de Barcelona, CSIC, Spain
4. Nanochemistry Research Inst., Curtin Univ. of Technology, Perth, Australia
5. Dept. de Ciencias de la Tierra y Física de la Materia Condensada, Univ. de Cantabria, Santander, Spain
6. Centre d'Investigació en Nanociència y Nanotecnologia (CSIC-ICN), Barcelona, Spain
7. Centro Mixto CSIC-UPV, Fac. Química, San Sebastián, Spain

We present recent developments around the SIESTA method of first-principles simulation. Topics covered include the implementation in the SIESTA code of a multigrid solver for the Poisson equation to allow flexibility in boundary conditions, a filtering procedure to reduce space-rippling effects, and a non-local exchange-correlation functional for dispersion interactions. We also discuss the status of the TranSiesta electronic-transport utility, and of other efforts aimed at improving the interoperability and post-processing abilities of the SIESTA package and its overall (parallel) performance.

Main Topic: T11 Other methods

Lattice dynamics study of high pressure phase transition in SiO_2

D. Kirin[1], I. Lukačević [2],

1. Rudjer Bošković Institute, P. O. B. 180, 10002 Zagreb, Croatia;
e-mail: kirin@irb.hr
2. Department of Physics, University of J. J. Strossmayer, 31000 Osijek, Croatia;
e-mail: ilukacevic@fizika.unios.hr

The pressure induced phase transition from the high pressure tetragonal structure of SiO2, stishovite (space group $P4_2/mnm$), to the highest observed form of orthorhombic structure ($CaCl_2$) has been controversial for many years. With the advent of high pressure experimental techniques, the phase transition pressure was put in the range of 50 GPa. The Raman experiments at high pressures [1] give the pressure of 50 GPa, and the structural studies predict the transition pressure of 54 GPa [2]. The transition from stishovite (rutile structure) to $CaCl_2$ structure is found to be accompanied with no or very small volume change (less than 1%), and experiments reveal that it is completely reversible.

All previous attempts to explain the mechanism of the phase transition were based on the assumption that there is a soft optical mode driving the transition, but in previous experiments only partially soft mode was observed in Raman spectrum [1]. The previous structural experiments [2] put forward the idea that the order parameter of the transition is an orthorhombic distortion $(a-b)/a$ of the tetragonal structure. It means that, at pressures higher than transition pressure, there is a distortion $(a-b)/a$ different from zero, and that actual symmetry is orthorhombic (space group $Pnnm$). Below the transition pressure $a = b$, and the structure is tetragonal (rutile structure $P4_2/mnm$). The Landau theory of phase transitions, with primary order parameter being crystal strain [3], gives certain predictions about the evolution of physical values with temperature or pressure. In that case the fluctuations of the order parameter are acoustic modes [3].

We calculated the lattice dynamics of the tetragonal phase as a function of pressure, using density functional perturbation theory (DFPT) [4] as implemented in ABINIT program package [5]. The results of the lattice dynamics calculations point the phase transition pressure around 39 GPa. At that pressure the frequency of the long wave transversal acoustic mode, along $(\xi, \xi, 0)$ direction in the Brillouin zone, becomes imaginary, i.e. the lattice is unstable with respect to such a distortion.

References

[1] K. J. Kingma, R. E. Cohen, R. J. Hemley and H. K. Mao, Nature **374**, 243 (1995).

[2] D. Andrault, G. Fiquet, F. Guyot, M. Hanfland, Science **282**, 720 (1998).

[3] R. A. Cowley, Phys. Rev. B **13**, 4877 (1976).

[4] X. Gonze, Phys. Rev. B **55**, 10337 (1997);
S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozi, Rev. Mod. Phys. **73**, 515 (2001).

[5] ABINIT is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (www.abinit.org).

Main Topic: T11 Other methods

Path-Integral Renormalization Group Method for Multicomponent Coulombic Systems

Masashi Kojo and *Hirose Kikuji*

Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita,
Osaka 565-0871 Japan

An accurate method to treat multicomponent systems within Path-Integral Renormalization Group (PIRG) method is proposed. It is based on the auxiliary-field technique and the non-orthogonal multi-Slater determinant, and can treat strongly-correlated electron systems with a comparatively few Slater determinants and without the sign problem. The PIRG method was originally proposed for model systems owing to the auxiliary-field [1]. And recently we extended it to be applicable to more realistic electron systems with long-rage repulsive coulomb interactions [2]. In the present work, further extension is applied to treat multicomponent systems, in which many disparate quantum particles interact with each other.

In the PIRG method, the many-body wave function is approximated with the linear sum of non-orthogonal Slater determinants and the ground state is swept out by the imaginary-time propagator. However, because two-body operators in the imaginary-time propagator rapidly increase the dimension of Slater determinant subspaces, the two-body operators have to be decomposed in terms of one-body operators by the auxiliary-field technique. This is why an appropriate auxiliary-field is necessary in the PIRG method.

To handle multicomponent systems with long-range repulsive coulomb interactions, we extended the auxiliary-field and applied it to a small system which contains two kinds of disparate quantum particles to check its validity.

[1] Kashima T, Imada M. J. Phys. Soc. Jpn. 70 (2001) 2287

[2] Kojo M, Kikuji H. Surf. Int. Anal. 40 (2008) 1071

Main Topic: T11 Other methods

Maximally localized Wannier Functions in Siesta

Richard Korytár[1]*, Javier Junquera*[3]*, Nicolás Lorente*[2]*, Pablo Ordejón*[2]*,*
Miguel Pruneda[2]

1. ICMAB (CSIC), Campus UAB, Bellaterra, Barcelona, Spain
2. CIN2 (CSIC,ICN), Campus UAB, Bellaterra, Barcelona, Spain
3. Dept. CITIMAC, Universidad de Cantabria, Santander, Spain

For a long time Wannier functions were only considered as a formal tool - mainly due to their non-uniqueness. The method of maximal localization introduced by Marzari and Vanderbilt opened the door to a variety of applications in insulators and molecules. In metals, the procedure of disentanglement (Souza, Marzari, Vanderbilt) allows for projecting the electronic states onto a subspace of maximally localized Wannier functions (MLWF) describing the electronic properties for a given interval of electron energies. Both strategies were implemented in the electronic structure post-processing program Wannier90 . One of its advantages is that the only input it requires, for the construction of MLWF, has the form of matrices of Bloch function overlaps, thus making no explicit reference to the particular basis set that was employed in the initial electronic structure calculation.

Our aim is to write these overlap matrices in Siesta in order to exploit the full functionality of Wannier90. Siesta is a first principles simulation package, whose distinctive feature is the use of a localized basis set of atomic-like functions. The present state-of-the-art interface between Siesta and Wannier90 allows to obtain MLWF for insulators and molecules and plot them in the real space.

Main Topic: T11 Other methods

Assessment of the quality of empirical potentials for small gold clusters

<u>Luis Mancera</u>[1], *David M. Benoit*[1],

1. Nachwuchsgruppe Theorie - SFB 569, University of Ulm,
Albert-Einstein-Allee 11, D-89081 Ulm, Germany

Most comparative studies of empirical potentials focus usually on analyzing how minimum structures reproduce minima obtained with higher level methods. The usual comparisons include binding energies, bond lengths and sometimes harmonic frequencies. Such analyses provide a useful description of the potentials, but these quantities alone do not guarantee a faithful representation of the high-level potential energy surface (PES). A direct comparison of empirical potentials is difficult since they have often different analytical expressions and their empirical parameters are not all fitted to the same experimental quantities. In this contribution, we present a new approach, based on a local comparison of PES around a given minimum structure, as an alternative way of assessing the quality of empirical potentials. The method uses a many-body expansion of the PES in terms of normal coordinates. This allows us to determine in a systematical way the features of the PES in the vicinity of a given minimum structure for each empirical potential. We compare the Murrell-Mottram, Sutton-Chen, Gupta, Glue and Voter-Chen potentials to results obtained with density functional theory (DFT), in particular the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and a Vanderbilt pseudopotential. The present study is carried out on neutral gold clusters with up to ten atoms.

T11: Other methods

A new Virtual Crystal Approximation approach

R. Poloni, J. Iñiguez, A. Garcia and E. Canadell

Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, E-08193 Bellaterra, Barcelona, Spain

It is well known that the VCA provides an efficient method for studying disordered alloys and solid solutions by first-principles. Within the VCA, the alloy compound is treated as a virtual crystal composed of virtual atoms obtained by compositionally averaging the pseudopotentials of the real component atoms. Many applications show that physical properties not strongly dependent on atomistic details, ranging from the electronic density of states of doped semiconductors to the piezoelectric properties of materials like $PbZr_{1-x}Ti_xO_3$, can be addressed successfully within the VCA.

Recently there have been attempts to use the VCA to predict partial ordering in solid solutions. All such attempts were based on the minimization of the energy of the virtual crystal as a function of the relevant variables describing the (dis)order (e.g., occupations of the relevant sites). However, we have found that the energy differences between different virtual compositions are not generally trustworthy, and it is not clear whether more sophisticated VCA schemes [1,2,3] can solve this problem.

Here we present an alternative VCA approach to study ordering problems. We show that, by making use of a minimal amount of experimental information, it is possible to define convenient figures of merit that allow a meaningful comparison between different virtual compositions. For example, we can impose the experimental unit cell in our calculations and look for the atomic structure and partial occupations that minimize the computed stress tensor. We have applied this approach to a variety of well characterized materials, ranging from oxynitrides to borocarbides and perovskites, and show that it predicts the experimental solution in all cases.

[1] L. Bellaiche and D. Vanderbilt, Phys. Rev. B 61, 7877 (2000);
[2] N. J. Ramer and A. M. Rappe, Phys. Rev. B 62, R473 (2000);
[3] C.-J. Yu and H. Emmerich, J. Phys.: Condens. Matter 19, 306203 (2007).

Main Topic: T11 other methods

Experimental and theoretical study of the polarized infrared spectral density of the hydrogen bond in 2-thiophenic acid crystal.

Najeh Rekik[1,2], *Houcine Ghalla*[1], *Brahim Oujia*[1], *Henryk T. Flakus*[3],

1. Laboratoire de Physique Quantique, Faculté des Sciences de Monastir, 5000 route de Kairouan, Tunisia.
2. Department of science, college of education, University of Hail, P. O. Box 1888, Hail 81472, Saudi Arabia.
3. Institute of Chemistry, University of Silesia, 9 Szkolna Street, Pl-40-006 Katowice, Poland.

Abstract

This paper presents the results of the experimental and theoretical study of the υ_{O-H} and υ_{O-D} band shapes in the polarized infrared spectra of 2-thiophenic acid crystals measured at room temperature and at 77K. We have applied a previous quantum model [rekik et al. submit to Chem. Phys] which took into account strong anharmonic coupling, Davydov- coupling, Fermi resonance, direct and indirect damping and the selection rule breaking mechanism for forbidden transitions in IR. In this model, the adiabatic approximation allowing to separate the high frequency motion from the slow one of the H-bond bridge is performed for each separate H-bond bridge of the dimer and a strong nonadiabatic correction is introduced into the model via the resonant exchange between the fast-mode excited states of the two moieties. Besides, the present approach reduces satisfactorily too many models in the literature dealing with more special situations. It correctly fits the experimental lineshape of the hydrogenated compound and predicts satisfactorily the evolution in the line shapes with temperature and the change in the line shape with isotopic substitution. The spectral density is obtained within the linear response theory by Fourier transform of the damped autocorrelation functions. The evaluated spectra are in fairly good agreement with the experimental ones by using a minimum number of independent parameters. The impact of the temperature is also well reproduced.

Keywords: H-bond; Infrared spectral density; Morse potential; Davydov coupling; Quantum direct and indirect damping; Fermi resonances; 2-thiophenic acid crystal.

Main Topic: T11 Other methods

Atomic-like basis functions in the Projector Augmented Wave method

M. Vanin[1], *A. H. Larsen*[1], *J. J. Mortensen*[1], *K. S. Thygesen*[1], *K. W. Jacobsen*[1]

1. Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark,DK - 2800 Kgs. Lyngby, Denmark.

We include the possibility to work with compactly supported atomic-like basis functions as an alternative to the grid-based finite-difference approach in the GPAW[1] code . The grid- and localized basis methods complement each other: with the grid-based scheme the complete basis set limit can be systematically reached while the localized basis allows for fast calculations in situations where efficiency is more important than high accuracy. Moreover, the localized basis is well suited for quantum transport calculations, linear-scaling computation schemes, molecular dynamics simulations, as well as for analysis purpose. To our knowledge GPAW is the first code combining localized basis functions with the Projector Augmented Wave (PAW) method, *and* the first code supporting two different, complementary basis sets within the same unifying framework, that is, with exactly the same set of approximations. Benchmark results against the grid are carried out to evaluate the accuracy of the basis sets.

---

[1] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Physical Review B, Vol. 71, 035109, 2005

Main Topic: A1 Nanoscience

Electronic structure of metalated DNA and xDNA base pairs by DFT

Giorgia Brancolini, *Rosa Di Felice*

National Research Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR, c/o Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A, 41100 Modena, Italy

The electronic properties of several metal-modified Watson-Crick guanine-cytosine (GC) base pairs and their size-expanded (xGC) [1] counterparts are investigated by means of first-principle density functional calculations. The modifications induced on the electronic structure by the water solvent are taken into account. Our study includes extensive tests of the exchange-correlation functionals and basis sets.

Since there are big expectations that metal doping of DNA can produce good molecular wires, we have recently carried out [2] a comparison of behaviors of different metal cations binding Watson-Crick guanine-cytosine base pairs. The results reveal the establishment of covalent bonding between the metal cation and the G and xG bases in suitable conditions. We discuss how and to which extent the complexation with transition metal ions and the presence of the solvent induce tuning of the energy levels and HOMO-LUMO gaps of GC and xGC pairs. In both natural and size-expanded base-pairs, Cu(II) is the cation species that mostly reduces the HOMO-LUMO gap, and the effect of the solvent is small. This gap reduction, along with the persistent planarity and strong Cu-G mixing of electron charge, indicate that Cu-modified GC and xGC complexes are the best candidates for nanowires with enhanced electron transfer and also for on-purpose modification of DNA double-helix for signal detection. We additionally note a general shrink of the HOMO-LUMO gap in complexes with Ag(I). In the case of Ag(I) complexes, the effect of guanine size expansion is larger than in the case of Cu(II) for what concerns electronic level shifts.

[1] Krueger A.T., Lu H., Lee A.H., Kool E.T., Acc. Chem. Res., **2007**, 40, 141
[2] Brancolini G., Di Felice R., J. Phys. Chem. B, **2008**, *112* (45), 14281-14290

Main Topics: A1 Nanoscience, A3 Magnetism and Spintronics

Electronic properties of boron nitride nanoribbons

Xavier Declerck[1,2], *Simon Dubois*[1,2], *and Jean-Christophe Charlier*[1,2]

1. Unité de Physico-Chimie et de Physique des Matériaux (PCPM),
Université Catholique de Louvain,
1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium
2. European Theoretical Spectroscopy Facility (ETSF)

Carbon-based nanostructures have been extensively studied during the past few years. However, boron nitride (BN) which presents a strong structural analogy to carbon at the macroscopic level (cubic or hexagonal BN) has been less investigated at the nanoscale although synthesized experimentally (BN fullerenes and BN nanotubes). These observed BN nanostructures always exhibit semiconducting behaviors. Recently, the field emission properties of porous BN nanourchins have been measured [1], suggesting for the first time the possibility of metallic BN nanoribbons.

BN nanoribbons are investigated using the density functional theory within the local spin density approximation as implemented in the *ABINIT* code. The electronic properties of BN ribbons presenting similar widths are predicted for various shaped edges (zigzag and armchair). When the edge of the BN ribbon is passivated with hydrogen, it exhibits a semiconducting behavior. However, when the edges are not passivated, zigzag BN nanoribbons are found to be metallic [2]. Furthermore, when spin effects are taken into account, two stable spin-polarized configurations (ferromagnetic ↑↑ and antiferromagnetic ↑↓) are stabilized at the edges of the ribbon. At last, in order to investigate the transport properties of these BN ribbons, transmission functions are predicted in an energy range close to the Fermi level, suggesting the use of these BN one-dimensional systems as spin-valve nanodevices.

[1] M. Terrones *et al.*, Nano Lett. **8**, 1026-1032 (2008).
[2] X. Declerck, S.M.M. Dubois, and J.-C. Charlier, in preparation (2008).

Main Topic: A1 Nanoscience

Microscopic crystalline stability of SiC, III-V, and II-VI crystals in the context of high- power/high-temperature applications

Paweł Jakubas, Piotr Bogusławski

Institute of Physics PAS, 02-668 Warsaw, Al Lotników 32/46, Poland

Study of Frenkel pairs (FPs), i.e., of vacancy-interstitial pairs, is an important research area since the beginning of the inquiry of defects in solids. Recently, interest has been devoted to diffusion, recombination, and interaction of FPs in Si [1, 2], ZnO [3] and graphite [4]. Generation of FPs may also explain resistive switching and ferroelectric-like behavior of CdZnTe alloys [5].

Applications of semiconductors in high-power/high-temperature devices require their structural robustness. Formation of FPs is one of the main mechanisms limiting structural stability under extreme conditions. Here, we investigate generation of FPs in both the wide band-gap SiC, GaN, and ZnO that are currently considered in the context of applications in high-power conditions, and in 'classical' CdTe, ZnTe, and GaAs. First principles calculations were based on the ESPRESSO code.

Our results allow identifying the main factors that determine mechanism and energy barriers for generation of FPs, which are (i) the sublattice on which FP is generated, (ii) the presence of free carriers, and (iii) local coordination of atoms, very different in the zinc-blende and in the wurtzite structure. In particular, we find that:

(i) In zinc-blende crystals, generation of FPs on cation sublattice is a few orders of magnitude more efficient than on the anion sublattice.

(ii) The presence of free carriers lowers the energy barriers, thus enabling the generation of FPs. Si, SiC, and GaAs are structurally stable, since the barriers of about 5-10 eV prohibit formation of FPs. In contrast, in the presence of excess electrons in CdTe and ZnTe the barriers may be as low as 1.4 eV, leading to a generation of FPs and to formation of 'dark defects' in II-VI light emitting diodes.

(iii) In intrinsic wurtzite GaN and ZnO, the corresponding barriers for the formation of FPs are high, 8.5 and 5.5 eV. The presence of free holes substantially lowers the barriers in ZnO to about ~1.0 eV. Consequently, in contrast to SiC and GaN, ZnO can be structurally unstable with respect to FP formation in high-power conditions, which may prevent its applications.

A comprehensive discussion of the obtained results based on the electronic structure of vacancies and interstitials is given.

Research supported in part by the Ministry of Science and Education N50703131/0743, and by the European Community - Research Infrastructure Action under the FP6 Programme (Project HPC-EUROPA++: RII3-CT-2003-506079).

[1] G. Watkins, in *Properties of Crystalline Silicon*, edited by R. Hull (The Institute of Electrical Engineering, London, 1997), pp. 641–652; P. Ehrhart and H. Zillgen, in *Defects and Diffusion in Silicon Processing*, MRS, San Francisco, 1997, Vol. 469, pp. 175–186; P. Partyka *et al.*, Phys. Rev. B **64**, 235207 (2001).
[2] M. J. Beck, L. Tsetseris, and S. T. Pantelides, Phys. Rev. Lett. 99, 215503 (2007).
[3] S. Vlasenko and G. D. Watkins, Phys. Rev. B 72, 035203 (2005).
[4] C.P. Ewels et al., Phys. Rev. Lett. 91, 025505 (2003).
[5] P. Jakubas, P. Boguslawski, Phys. Rev. B **77**, 214104 (2008); T. Wojciechowski, P. Jakubas, P. Bogusławski, and G. Karczewski, J. of Korean Phys. Soc. **53** (1): 23-27 Jul 2008.

Main Topic: A1 Nanoscience

Doping graphene with metal contacts

P. A. Khomyakov[1], *G. Giovannetti*[1,2], *P. C. Rusu*[1], *G. Brocks*[1], *V. M. Karpan*[1], *J. van den Brink*[2,3], *P. J. Kelly*[1]

1. Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
2. Instituut-Lorentz for Theoretical Physics, Universiteit Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands
3. Institute for Molecules and Materials, Radboud Universiteit, Nijmegen, The Netherlands

Since electronic transport measurements through a graphene sheet require contacts to metal electrodes it is essential to have a full understanding of the physics of metal-graphene interfaces. We study how graphene is doped by adsorption on metal substrates using *ab-initio* density functional theory [Phys. Rev. Lett. **101**, 026803 (2008)]. We find that weak bonding on Al, Ag, Cu, Au and Pt, while preserving its unique electronic structure, can still shift the Fermi level with respect to the conical point by ~ 0.5 eV. At equilibrium metal-graphene separations, the crossover from p-type to n-type doping takes place for a clean metal surface work function of ~ 5.4 eV that is much larger than the work function of 4.5 eV for free-standing graphene.

We propose a simple analytical model that describes the numerical results for the Fermi level shift in graphene and work function of graphene-covered metal surfaces solely in terms of the clean metal surface work function. The model provides a general description of doping, and can be applied to a variety of other metals, greatly extending the applicability of our numerical results.

We also find a class of metals such as Co, Ni, Pd and Ti that strongly absorb graphene. Graphene p_z-states are hybridized with d-states of the metal surfaces. The chemisorption then leads to a large bandgap opening in graphene and to decrease of the clean metal surface work function much lower than the work function of free-standing graphene. Based on the latter observation, we consider graphene absorbed upon Co, Ni, Pd and Ti as being n-type doped.

Main Topic: A1 Nanoscience

Ab-initio study of Cd vacancy and impurity doping in CdTe clusters

Somesh Kr. Bhattacharya[1,2] *and Anjali Kshirsagar*[1]

1. Department of Physics, University of Pune, Pune 411 007, India
2. Currently at AS ICTP, Trieste, Italy

We study Cd vacancy formation in stoichiometric and non-stoichiometric CdTe clusters having zincblende and wurtzite symmetry with and without passivation. For certain clusters like $Cd_{12}Te_{16}$, vacancy leads to severe distortion of the geometry due to propagation of the defect. Passivated clusters retain their initial geometry and vacancy induced structural distortion is not seen in these clusters as the defect gets localized. Vacancy induces intragap states in these clusters. However, it is observed that passivation of the dangling bonds, created by the vacancy, removes these intragap states. The values of vacancy formation energy in these clusters show that except for $Cd_{12}T_{16}$ all other clusters resist vacancy formation as it reduces their stability. Creation of vacancy is found to be easier at the center than on the surface of a cluster.

Semiconductor compounds will not be useful if enough charge carriers are not generated in them at room temperature. This can be achieved by doping them with suitable impurity atoms. We therefore substituted a Cd atom by Pd/Ag/In/Sn in these CdTe clusters and found that doping by metal atoms increases the stability. For certain clusters, metal atom doping leads to a half metallic character. The most interesting structural change is exhibited by $Cd_{12}T_{16}Pd$. The T_d symmetry is completely lost. The relaxed geometry is comprised of two units of Cd_6Te_8 bridged by the Pd atom. Doping is found to be easier in larger clusters. Pd/Ag doped clusters are *p*-type semiconductors where as In doped clusters are *n*-type semiconductors. Sn doping in these clusters does not result in *n*-type semiconductor. A comparison of earlier studies on CdSe clusters and the present work on CdTe clusters suggests that CdTe clusters may be ideal candidates for doping to fabricate junction devices. Localized moments and half-metallic character suggest that these clusters can be used as building blocks for new materials for application in optoelectronic devices.

Main Topic: A1 Nanoscience

Applications of First Principles calculations to Oil & Gas industry

Caetano R. Miranda[1] and Toshifumi Matsuoka[1]

1. Dept. Civil and Earth Resources Engineering - Kyoto University – Kyoto - Japan

Nanogeoscience is emerging as a new discipline bringing together two very distingue scales of length: the micro (atomic at nanoscale) and the macro World. A fundamental question would be how the effects on the atomic scale can drive phenomena at macro scale and its applications involve several fields: Enviromental and Soil Sciences, Mining and Energy. In this work in extension to our series “Ab-initio for a better World”, we present a series of applications of Nanogeoscience through atomistic simulations. From First Principles calculations to the use of Classical Interatomic potentials with Molecular Dynamics and lattice Boltzmann simulations, we have been able to address and explore several issues on Mining and Oil & Gas industry. This plethora of phenomena ranges from the determination of elastic constants of Clathrate hydrates with guest molecules, opening the possibility to estimate the amount of methane and CO2 in hydrate reservoir; the study of wettability phenomena for enhanced oil recovery (EOR) applications through simulations of nanodroplets of crude oil on a SiO_2 surface under H_2O solution in order to determine the surface tension and the contact angle to the effect of CO2 in concrete and the study of cement at nanoscale, which may lead to improvement in the cement properties. By better understanding a) oil-water-rock interface interactions at molecular level, b) the absorption and desorption of hydrocarbon and CO2 molecules on surfaces of rocks and c) the wettability under different conditions (ambient and reservoir), it is possible from first principles calculations to explore and evaluate new directions to improve Enhanced Oil recovery (EOR) and geological CO2 sequestration.

Main Topic: A1 Nanoscience

Tayloring nano and meso oxide structures for energy applications

Tomohiro Kabashima[1], *Dai Makimura*[1] *and* *Caetano R. Miranda*[1]

1. Dept. Civil and Earth Resources Engineering - Kyoto University – Kyoto - Japan

Energy generation has become a very important issue from global to nanoscale. Worldwide, a considerable interest has been given for a clean renewable energy generation and efficient oil recovery. At the same time, the necessity to supply energy to nanodevices adds a huge technological challenge. In both scales, nano- and meso-structured oxides devices are expected to give considerable contribution. Oxides can act as filters for CO_2 capture in a clean Hydrogen production and it is also the basis of solar cell devices. Furthermore, nanostructured oxides may be used as power suppliers to nanodevices due to their piezoelectric properties. Besides its technological importance, very little is known about the mechanical and thermodynamic stability of meso and nano oxides. In this work, our purpose is to design new nano and meso oxide structures for energy applications. We have applied Molecular Dynamics (MD) to obtain the thermal and mechanical properties of mesoporous MgO and SiO_2 nanotubes. The mesoporous oxides were generated by creating spherical voids with different radii inside the oxide matrix and minimizing its surface area and energy. Silica nanotubes with different lengths and radii have been generated based on ab-initio data. The structures were optimized by steepest descent method and their physical properties obtained by MD. The well-tested Tangney-Scandolo potential based on fluctuating dipole model was used to describe SiO_2 and Mg. We found the optimal energy structures for both mesoporous system and nanotubes. For mesostructured MgO and SiO2, we study the effect of spherical void diameter on the structure stability. For SiO2 nanotubes, the mechanical (Young Modulus and Poisson ratio) and thermodynamic (melting point and thermal expansion coefficient) properties have been obtained and the piezoeletric was further explored by using First Principles calculations. The Young modulus decreases with the increasing SiO_2 molecule per ring. The calculations also reveal the importance of O-bridge atoms on the thermal and mechanical properties. Unusual properties such as negative Poisson ratio and apparent negative thermal expansion have been observed. Our findings suggest a potential use of silica nanotubes as mechanical absorbent and nanostructured electric generator. Additionally, the thermal stability of taylored spherical amorphous nanostructures has been investigated for Enhanced Oil Recovery applications.

Main Topic: A1 Nanoscience

Investigating Defects in Semiconductors using *Ab Initio* Random Searching

Andrew J. Morris[1], Chris J. Pickard[2] Richard J. Needs[1]

1. Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom.
2. Scottish Universities Physics Alliance, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom.

The *ab initio* random searching (AIRS) technique has recently produced new structures of high-pressure phases of materials. These have since been discovered in experiment [1,2].

The AIRS method has now been modified to search for point defects in semiconductors. Defects in crystalline silicon consisting of a silicon self-interstitial atom and one, two, three, or four hydrogen atoms are studied within density-functional theory. We search for low-energy defects by starting from an ensemble of structures in which the atomic positions in the defect region have been randomised. We then relax each structure to a minimum in the energy. We find a new defect consisting of a self-interstitial and one hydrogen atom (denoted by $\{I, \mathrm{H}\}$) which has a higher symmetry and a lower energy than previously reported structures. We recover the $\{I, \mathrm{H}_2\}$ defect found in previous studies and confirm that it is the most stable such defect. Our best $\{I, \mathrm{H}_3\}$ defect has a slightly different structure and lower energy than the one previously reported, and our lowest energy $\{I, \mathrm{H}_4\}$ defect is different to those of previous studies. A study of which defects are most prevalent at zero and finite temperature is presented.

We also present the multi-B method of k-point sampling and show its advantage over standard Monkhorst-pack schemes.

[1] Chris J. Pickard and R. J. Needs. Phys. Rev. Lett. **97**, 045504 (2006).
[2] Chris J. Pickard and R. J. Needs. Phys. Rev. B **76**, 144114 (2007).
[3] Andrew J. Morris, Chris J. Pickard and R. J. Needs. *"Hydrogen/silicon complexes in silicon from computational searches."* Phys. Rev. B **78** 184102 (2008).

Main Topic: A1 Nanoscience

Embedded cluster model for the study of the electronic structure and spectroscopic properties of cubic ZrO_2 nanocrystallites.

David Muñoz Ramo[1], *Peter V. Sushko*[1,2], *and Alexander L. Shluger*[1,2]

1. Department of Physics and Astronomy and the London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, UK
2. WPI Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, 980-8577 Japan.

Pure and doped ZrO_2 is used in a large number of applications ranging from heterogeneous catalysis and fuel cells to oxygen sensors and electronic devices. Most applications of ZrO_2 are based on properties of its less stable tetragonal and cubic polymorphs stabilized either by doping or size confinement as in thin films and nanocrystals. In this material oxygen vacancies are the dominant intrinsic defects, which affect its chemical, mechanical, electric and optical properties, and play a role in stabilizing the cubic phase over the monoclinic phase at room temperature. Issues like the distribution of vacancies and dopants and interpretation of associated spectroscopic data are still being debated. In addition, theoretical interpretation of spectroscopic data concerning ZrO_2 nanoparticles still has not been addressed.

We present an embedded cluster methodology developed in our group to study defect properties in ZrO_2 cubic nanoparticles. This technique allows us to predict spectroscopic defect properties for comparing with experimental data and identifying the defect structure. In this model, the system is roughly divided in three regions, a quantum mechanical region and two classical regions, polarizable and nonpolarizable, that represent the electrostatic influence of the whole crystal on the quantum mechanical cluster. Accurate classical pair potentials have been developed for the description of this classical region and its interaction with the quantum cluster, which take into account the electrostatic Coulomb potential and the short-range polarization through a simple shell model. The accuracy of the method is tested through a detailed comparison of the atomic and electronic structures of the perfect lattice and defect properties with the results of periodic calculations. Five stable charge states have been found for the oxygen vacancy. These states span localized levels in the middle of the gap (V^+, V^0, V^-, V^{2-}) and near the conduction band (V^+, V^-, V^{2-}). Their spectroscopic properties have been characterized in order to provide guidance to possible experimental measurements.

Main Topic: A1 Nanoscience

Cu adsorption on H-passivated Si(001) surface with Bi nanolines: a first-principles analysis

A. Rodriguez-Prieto[1,2], D. R. Bowler[1,2,3],

1. London Centre for Nanotechnology, University College London
2. Materials Simulation Laboratory, University College London
3. Department of Physics and Astronomy, University College London

We have analyzed, by means of first-principles analysis, the adsorption of Cu adatoms on the Hidrogen passivated Si(001) surface with self-assembled Bi nanolines. In spite of Cu is a fast diffuser in bulk Si, we prove that it preferentially migrates towards the surface in the proximities of the nanolines. Adsorption of Cu at the nanolines and their surroundings has been studied in detail, and we can conclude that the adatoms nucleate at the backbond sites of the nanoline. The migration route from bulk Si towards the surface and the backbond sites is also analyzed, as well as possible backbond migration routes through backbond sites which could lead to a posibble dimer formation.

Main Topic: A1 Nanoscience

Adsorption of CO on monatomic wires: a comparison between Pt and Au

G. Sclauzero[1,2], *A. Dal Corso*[1,2], *A. Smogunov*[2,3,4], *and E. Tosatti*[1,2,3]

1. International School for Advanced Studies (SISSA-ISAS), Trieste (Italy)
2. CNR-INFM Democritos, Trieste (Italy)
3. International Centre for Theoretical Physics (ICTP), Trieste (Italy)
4. Voronezh State University, Voronezh (Russia)

Recent experiments addressed the effect of a CO molecule on the ballistic conductance of Au, Cu, Pt and Ni atomic contacts, showing that the molecule modifies the break junction conductance histograms in a peculiar way for each metal [1]. CO interacts both with Pt and Au nanojunctions, but the changes in the histograms look very different for the two metals and still lack of a comprehensive interpretation. We investigate the electronic structure and ballistic conductance of these systems by studying, within density functional theory, an idealized model made of one CO molecule adsorbed on an infinite straight monatomic chain of platinum [2] or gold. We compare the two metals and study the effect of the CO adsorption site (top or bridge) on the ballistic conductance. We find that, for both Pt and Au, the molecule prefers to attach at the bridge site of the chain and that the binding involves a Blyholder-like donation/back-donation mechanism between the molecule and the metal. The transmission of s electrons is characterized by some dips at specific energies which depend on the details of the interaction, which in turn depends on the metal, on the adsorption site and also on the strain of the wire. Spin-orbit coupling influences substantially the band structures of Pt and Au chains, but perturbs only slightly these features. If these dips appear at the Fermi energy, a strong reduction in the conductance is expected for the Au chain, where only s electrons are present at that energy. Actually this happens for a strained configuration with CO ontop (as previously found by others [3]), and can be directly related to the donation of molecular σ states. However, a smaller strain or a different adsorption site can spoil this effect and restore larger values of conductance. The study of the effects of more realistic atomic configurations (a short wire between tips/surfaces) on these conclusions is in progress.

References

[1] M. Kiguchi *et al.*, Nanotechnology **18**, 035205 (2007).
[2] G. Sclauzero *et al.*, Phys. Rev. B **78**, 085421 (2008).
[3] A. Calzolari *et al.*, Phys. Rev. Lett. **93**, 096404 (2004).

Main Topic: A1 Nanoscience

Conductance eigenchannels and density of states for an open quantum system: the case of monatomic wires with an impurity

A. Smogunov[1,2,3], *A. Dal Corso*[2,4], *and E. Tosatti*[1,2,4]

1. International Centre for Theoretical Physics (ICTP), Trieste (Italy)
2. CNR-INFM Democritos, Trieste (Italy)
3. Voronezh State University, Voronezh (Russia)
4. International School for Advanced Studies (SISSA), Trieste (Italy)

The Landauer-Büttiker conductance through a nanoconstriction can be conveniently written as a sum, $G = \sum_j G_j$, of contributions from independent conductance eigenchannels j. They are defined as linear combinations of scattering states diagonalizing both the transmission and reflection matrices [1] and transform according to the irreducible representations of the system symmetry group (containing the symmetry operations which keep the transport direction unchanged). The eigenchannels (or, equivalently, the scattering states) provide a natural basis for constructing the density of states of an open quantum system, free of spurious gaps and features obtained by assuming periodic boundary conditions in the transport direction. We implemented the calculation (and visualization) of the conductance eigenchannels and of the projected (onto different atomic orbitals) density of states (PDOS) within the plane-wave scattering code `PWCOND` (a part of the software package `Quantum-ESPRESSO` [2]). We note that the localized states which do not couple to the left and right leads can not be captured directly by our scattering approach but can be found by looking for singularity points (in energy) of some transfer matrix. As an example, we consider a monatomic Pt wire with an adsorbed CO molecule as a scatterer and show the charge density of conductance eigenchannels of different symmetries. The calculation of the PDOS and the plot of localized states is illustrated on a simple system – a monatomic Al wire with a H impurity. We show, in particular, that the PDOS obtained with periodic boundary conditions indeed displays many gaps due to artificial copies of H atom but approaches the one constructed with the scattering states upon significant increase of the number of Al atoms (~ 100) separating the H atoms.

References

[1] see, e.g., M. Brandbyge *et al.*, Phys. Rev. B **56**, 14956 (1997).
[2] http://www.quantum-espresso.org.

A1 Nanoscience

Effect of adsorbates on the isomer stability of Ir_4 clusters

Vladan Stevanović[1], *Željko Šljivančanin*[1,2], *Alfonso Baldereschi*[1,3]

1. Institute of Theoretical Physics and IRRMA, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
2. Interdisciplinary Nanoscience Center (iNANO) University of Aarhus, 8000 Aarhus C, Denmark
3. Dipartimento di Fisica Teorica, Università di Trieste, I - 34014 Trieste, Italy

The relative stability of Ir_4 isomers, both in the gas phase and on MgO(100) substrates, has been studied using density functional theory. The square Ir_4 isomer is the most stable in both cases. The metastable tetrahedral geometry, which experimental data suggest as the most stable form of Ir_4 on MgO(100), is highly distorted by the strong interactions with the surface oxygen. The relative stability of Ir_4 isomers is strongly altered by adsorption of a single C atom since the binding energy of the C adatom to tetrahedral and butterfly Ir_4 isomers is much larger ($\sim$ 1.7 eV) than that to square Ir_4, both in the gas-phase and on MgO(100). After carbon adsorption, the most stable structure of Ir_4 is the butterfly geometry for free clusters and the "tetrahedral" one for Ir_4/MgO(100). The C adatom binds in a bridge configuration in all cases and reduces, when compared to gas-phase Ir_4, the distortions produced by the MgO substrate. On the other hand, interaction with the atomic H, O or with a single CO molecule, that could also be present in those systems due to the preparation procedure, does not change the relative stability of the three isomers both in the gas phase and when supported by MgO(100).

Main Topic: A1 Nanoscience

Nanowires on Ge(001): a DFT study of Pt induced Ge nanowires.

Danny E. P. Vanpoucke[1], Geert Brocks[1]

1. Computational Materials Science, Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente

Pt deposited on a Ge(001) surface gives rise to the spontaneous formation of nanowire(NW) arrays after annealing at a temperature T= 1050K. These defect and kink free nanowires have a cross-section of a single atom and can be several hundred angstroms long. Their length is only limited by the underlying Pt-Ge surface, the β-terrace.[1]

We present an *ab-initio* density functional theory(DFT) study of the structure of the β-terrace and the nanowires [2]. We calculate the total energies and compare simulated scanning tunneling microscope(STM) images to experimental STM images to identify the most probable structures.

Our results show the β-terrace has a structure similar to the clean Ge(001) surface, but with one in four Ge surface atoms replaced by a Pt atom giving rise to a checkerboard pattern of Pt-Ge and Ge-Ge surface dimers [3].

The formation process of the nanowires is shown to be driven by the increase in the concentration of Pt in the surface layers. Most remarkably, we predict that the experimentally observed "platinum" NWs, in fact, consist of *germanium atoms*. These Ge NWs are located in the platinum lined troughs of a modified β-terrace. The (4×1) periodicity along the wire is caused by Pt atoms located in the trough, which bind to one of the nanowire-dimer-atoms.This bond also anchors the Ge NW dimers increasing the nanowire stability[3].

[1] O. Gurlu et al. ,*Appl. Phys. Lett.* **83**,4610 (2003)
[2] D.E.P. Vanpoucke and G. Brocks ,*Phys. Rev. B* **77**,241308(R) (2008)
[3] D.E.P. Vanpoucke and G. Brocks ,*in preparation*

Main Topic: A1 Nanoscience

First principles studies of semiconductor nanoparticle quantum dots

Brent Walker[1], Shaun Hendy[1,2], and Richard Tilley[2]

1. Industrial Research Limited, 69 Gracefield Road, P.O. Box 31-310, Lower Hutt, New Zealand
2. MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

Semiconductor nanoparticles are *tiny* pieces of material, having sizes in the approximate range 1-100 nm. At these scales, quantum-mechanical effects become increasingly important and result in nanoparticles exhibiting many properties markedly different from those of bulk materials. The effect of quantum confinement means semiconductor nanoparticles are a type of quantum dot (QD) and affords them striking optical properties, especially narrow, well-defined peaks in the optical spectra that can be tuned (by adjusting the QD size and surface termination) through a broad range of wavelengths. Practical applications of quantum dots in many areas are currently being researched; our motivation is their potential use as optical markers for tracking cells and disease in medical physics, a purpose for which their favorable optical properties and long lifetimes in cells (up to 100 times those of organic dyes conventionally used) make them particularly exciting, promising cell monitoring for days rather than hours.

In this work we model Si, Ge and Sn nanoparticles using first principles computer simulations based on density functional theory (DFT) and time-dependent density functional theory (TDDFT). These simulations allow us to predict the structural, electronic and optical properties of QDs on an accurate quantum-mechanical basis at an affordable computational cost. We are particularly interested in the influence that changing the surface functionality has on quantum dots and so consider how their properties vary upon changing the surface termination by attaching -OH, -CH3 and -NH2 functional groups. Optical absorption spectra have been calculated using recently-developed approaches [1][2] based on the application of Lanczos algorithms to the central equations of time-dependent DFT in the linear response (LR) regime. The efficiency of the Lanczos/LR-TDDFT approach allows high throughput calculations of the absorption spectra for many nanoparticle model configurations in a systematic study.

[1] B. G. W., A. M. Saitta, R. Gebauer, and S. Baroni, *Physical Review Letters*, **96**, 113001, (2006)

[2] D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, *Journal of Chemical Physics*, **128**, 154104 (2008)

Main Topic: A1 Nanoscience

Stability and Aromatic Structure of Graphene Nanoribbons

Tobias Wassmann[1]*, Ari P. Seitsonen*[1]*, A. Marco Saitta*[1]*, Michele Lazzeri*[1]*, Francesco Mauri*[1]

1. IMPMC, Campus Boucicaut, Université Pierre et Marie Curie, Paris, Paris

We analyze the stability, the geometry, the electronic and magnetic structure of hydrogen-terminated graphene-nanoribbons edges as a function of the hydrogen content of the environment by means of density functional theory. Antiferromagnetic zigzag ribbons are stable only at extremely-low ultra-vacuum pressures. Under more standard conditions, the most stable structures are the mono- and di-hydrogenated armchair edges and a zigzag edge reconstruction with one di- and two mono-hydrogenated sites. At high hydrogen-concentration "bulk" graphene is not stable and spontaneously breaks to form ribbons, in analogy to the spontaneous breaking of graphene into small-width nanoribbons observed experimentally in solution. The stability and the existence of exotic edge electronic-states and/or magnetism is rationalized in terms of simple concepts from organic chemistry (Clar's rule).

Main Topic: A2 Biochemistry and Biomaterials

Radiation damage of biomolecular systems: a first-principles molecular dynamics approach

Jorge Kohanoff[1,2], *Emilio Artacho*[2],

1. Atomistic Simulation Centre, Queen's University Belfast, UK
2. Department of Earth Sciences, Cambridge, UK

We present results of first-principles molecular dynamics simulations of carbon projectiles shooting through water in the liquid state in the adiabatic regime, where the electrons are always in the instantaneous ground state. Using the SIESTA code, we study a range of projectile velocities up to the estimated upper limit for the adiabatic approximation and analyze the different types of collision events. We show that for high projectile velocities collisions are mostly binary, but at lower velocities most trajectories exhibit a continuous energy loss to the medium, which cannot be properly described as a sequence of independent binary collisions. For the slowest projectiles we observe the formation of new chemical species such as hydronium, $H_5O_2^+$ and hydrogen peroxide. When the C-atoms are completely stopped, we also observe the formation of species like formic acid. By analyzing the generation of secondary fragments, we see that these are mostly hyperthermal and their spatial rate of generation increases with decreasing projectile energy. The two most numerous species are H and OH. We also show preliminary results for guanine solvated in water.

In a second part we study, via electronic dynamics with fixed nuclei, the opposite (sudden) regime of swift protons producing only electronic excitation in ice, under channeling conditions. We observe the existence of a threshold velocity for electronic excitation of about 0.2 a.u. By monitoring the rate of increase of the total energy, we calculate the electronic stopping power, and reproduce the experimentally observed maximum in electronic stopping at proton energies of about 70 keV. We also analyse the charge state of the projectile, the extent and localization of the deformation of the charge density, and the time scale for transient processes as a function of the projectile's velocity.

Main Topic: A2 Biochemistry and Biomaterials

Hydration of bioactive glass surfaces

Antonio Tilocca[1], *Alastair N. Cormack*[2]

1. Department of Chemistry, University College London (UK)
2. Inamori School of Engineering, Alfred University, NY (USA)

We have performed Car-Parrinello Molecular Dynamics simulations and structural optimizations of two model surfaces of a bioactive glass, with composition 45% SiO_2, 6% P_2O_5 and 24.5% of both Na_2O and CaO (wt %). The active surface sites were probed through their direct interaction with a water molecule: the water probe was released next to a specific site and then left free to locate a stable adsorption minimum by undamped and damped CPMD [1]. Three-coordinated Si atoms represent the strongest surface sites, able to induce spontaneous water dissociation at room temperature, provided that they are combined with a proton acceptor such as a nonbridging oxygen. Additional adsorption sites were located near to Na or Ca cations, which appear to be directly involved in the glass dissolution mechanism, by providing favorable pathways allowing water to penetrate under the surface. Small (2- or 3-membered) silica rings are also common features of the surface, not found in the bulk. The determination of minimum energy paths [2] shows that, despite a favourable energetic balance, opening of these rings upon water dissociation is hindered by a significant energy barrier. Given the availability of alternative, more favorable molecular adsorption sites, this effect can result in some of the small rings not being open and hydroxylated upon immersion in a physiological environment. This supports a recent hypothesis involving these rings as nucleation sites of dissolved Ca^{2+} and PO_4^{3-} ions in the initial stages of the bioactive fixation mechanism [3].

[1] A. Tilocca and A. N. Cormack, *J. Phys. Chem. C* **2008,** 112, 11936.
[2] Y. Kanai, A. Tilocca, A. Selloni and R. Car, *J. Chem. Phys.* **2004,** 121, 3359.
[3] N. Sahai and M. Anseau, *Biomaterials* **2005,** 26, 5763.

Main Topic: A3 Magnetism and Spintronics

An ab-initio description of correlated phases of cerium.

Bernard Amadon, François Jollet, Marc Torrent

CEA/DAM-Ile de France, 91297 Arpajon Cedex, France

We present an *ab-initio* description of the correlated phases of cerium. In accordance to previous results[1], we find that the LDA+U method improves the description of the γ phase. We show that the method applies also to the ground state of the β phase[2]. In particular, structural parameters and magnetism are improved. We describe the problem of the search for the ground state of the system in term of occupation matrices. We briefly discuss the LDA+U results with respect to more accurate LDA+DMFT calculations[3].

[1] A. B. Shick, W. E. Pickett, and A. I. Liechtenstein, J. Elec. Spec. Relat. Phen. **114-116**, 753 (2001).

[2] B. Amadon, F. Jollet, and M. Torrent, Phys. Rev. B **77**, 155104 (2008).

[3] B. Amadon, S. Biermann, A. Georges, and F. Aryasetiawan Phys. Rev. Lett. **96**, 066402 (2006).

Main Topic: A3 Magnetism and Spintronics

Graphite and Graphene as Perfect Spin Filters

V. M. Karpan[1], *P. A. Khomyakov*[1], *A. A. Starikov*[1], *G. Giovannetti*[1,2], *M. Zwierzycki*[1], *M. Talanana*[1], *G. Brocks*[1], *J. van den Brink*[2,3], *P. J. Kelly*[1]

1. Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
2. Instituut-Lorentz for Theoretical Physics, Universiteit Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands
3. Institute for Molecules and Materials, Radboud Universiteit, Nijmegen, The Netherlands

The in-plane lattice constants of close-packed planes of fcc and hcp Ni and Co match that of graphite almost perfectly so that they share a common two dimensional reciprocal space. Their electronic structures are such that they overlap in this reciprocal space for one spin direction only allowing us to predict perfect spin filtering for interfaces between graphite and (111) fcc or (0001) hcp Ni or Co [Phys. Rev. Lett. **99**, 176602 (2007); arXiv:0809.5168]. First-principles calculations of the scattering matrix show that the spin filtering is quite insensitive to amounts of interface roughness and disorder which drastically influence the spin-filtering properties of conventional magnetic tunnel junctions or interfaces between transition metals and semiconductors. When a single graphene sheet is adsorbed on these open *d*-shell transition metal surfaces, its characteristic electronic structure, with topological singularities at the K points in the two dimensional Brillouin zone, is destroyed by the chemical bonding. Because graphene bonds only weakly to Cu which has no states at the Fermi energy at the K point for either spin, the electronic structure of graphene can be restored by dusting Ni or Co with one or a few monolayers of Cu while still preserving the ideal spin injection property.

Main Topic: A3 Magnetism and Spintronics

Magnetism at the Gd/V interface

L. Mouketo[1], *B. M'Passi-Mabiala*[1], *N. Binggeli*[2]

1. GSMC, Department of Physics, Marien Ngouabi University, Congo
2. ICTP , Italy

Recent experimental investigation of magnetism properties of the Vanadium-Gadolinium (V/Gd) interface shows that Vanadium, which is nonmagnetic in the bulk, can acquire a magnetic moment in such systems. We have performed DFT *ab initio* calculations, with the pseudopotential plane-wave-self consistent field (PWscf) code. It is observed that V interface magnetic moments are aligned antiparallel to the Gd ones, as reported in experimental measurements [Backzewski et al., Phys.Rev. B, 74 (2006) 075417]. We discuss the different magnetic configurations and the possible mechanism that can produce the observed magnetic behavior in V film in the framework of the fundamental magnetic interactions namely the direct one through the d-d exchange interactions and the indirect one through RKKY interaction via valence electrons. We found that the 5d states contribution to the Gd moment is reduced at interface atoms compared to the bulk. This confirms that the coupling of moments is mediated by 5d state via the 4f-5d exchange and the 3d-5d hybridization as predicted in Gd/Co systems [Anilturk and. Koymen, Phys. Rev. B 68, 024430 (2003).].

P 0093

Main Topic: A3 Magnetism and Spintronics

On the Magnetism of Substitutional Transition-Metal Impurities in Graphenic Nanostructures

E. J. G. Santos, A. Ayuela, D. Sánchez-Portal
Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU and Donostia
International Physics Center (DIPC), Apdo. 1072, 2080 San Sebastián, Spain

We report a theoretical study of substitutional Ni, Co and Fe impurities in graphene. Only Co_{sub} defect is magnetic with a magnetic moment of ~1□$_B$ for the isolated impurity. However, when the Co substitution takes place in more than one site, the total magnetic moment of the system exhibits a strong dependency on the relative position of the Co_{sub} impurities. More precisely the magnetic moment depends on the number of Co substitutions in A and B sublattices. This behaviour is better understood when we realize that the electronic structure of a substitutitonal Co impurity nearby the Fermi energy is equivalent to that of a carbon vacancy in a simple □-tight-biding model of graphene. Therefore, we can expect the Lieb's[1] theorem to apply to this situation and the total magnetic moment to behave as $|Co_A-Co_B|$, where Co_A and Co_B are, respectively, the number Co substitutions in the A and B graphene sublattices [2].

In contrast to Co impurities, Ni_{sub} defects, which have been recently detected in carbon nanotubes by Ushiro *et al.*[3] using extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) data, show a zero magnetic moment in flat graphene. However, Ni_{sub} impurities develop a non-zero magnetic moment in metallic carbon nanotubes [4]. This surprising behavior stems from the peculiar curvature dependence of the electronic structure of Ni_{sub}. A similar magnetic/non-magnetic transition of Ni_{sub} can be expected by applying other kinds of anisotropic strain to a flat graphene layer [5].

In general, we have found that we can draw an analogy between the electronic structure in the neighborhood of the Fermi energy, and its strain dependence, of substitutional Co, Ni and Fe atoms in graphenic systems and that of an unreconstructed carbon vacancy in graphene with different charge states. With this analogy at hand we can easily understand and predict many complex and interesting phenomena for graphenic nanostructures substitutionally doped with transition metals.

[1] E. H. Lieb, Phys. Rev. Lett. **62,** 1201 (1989).
[2] E. J. G. Santos, D. Sánchez-Portal and A. Ayuela, in preparation.
[3] M. Ushiro, K. Uno, T. Fujikawa, Y. Sato, K. Tohji, F. Watari, W. J. Chun, Y. Koike, and K. Asakura, Phys. Rev. B **73,** 144103 (2006).
[4] E. J. G. Santos, A. Ayuela, S. B. Fagan, J. Mendes Filho, D. L. Azevedo, A. G. Souza Filho and D. Sánchez-Portal, Phys. Rev. B **78**, 195420 (2008).
[5] D. Sánchez-Portal, E. J. G. Santos and A. Ayuela, in preparation.

Main Topic: A3 Magnetism and Spintronics

Orientation and temperature dependence of the anomalous Hall effect in hcp cobalt

Ivo Souza[1], *Eric Roman*[1], *Yuriy Mokrousov*[1,2]

1. Department of Physics, University of California, Berkeley, USA
2. Institute of Applied Physics and Microstructure Research Center, University of Hamburg, Germany

We calculate from first-principles the evolution of the intrinsic anomalous Hall conductivity vector $\boldsymbol{\sigma}^a$ of hcp Co as the spin magnetization direction $\hat{\mathbf{M}}$ is tilted away from the c-axis. We find that $\boldsymbol{\sigma}^a$ varies smoothly with the tilt angle θ, and that its magnitude is strongly reduced between $\theta = 0$ and $\theta = \pi/2$: $r \equiv \sigma_z^a(0)/\sigma_x^a(\pi/2) \simeq 4$, in good agreement with the experimental value of $r \simeq 3$.[1] In addition to the anisotropic linear magnetization dependence ($\sigma_z^a/M_z \neq \sigma_x^a/M_x$) expected for any uniaxial crystal, there is a considerable nonlinearity in the dependence of σ_x^a on $M_x = M \sin\theta$, while the relation between σ_z^a and $M_z = M\cos\theta$ is essentially linear, as in other materials[2]. The overall angular dependence of $\boldsymbol{\sigma}^a$ is well-described by an expansion in terms of $l = 1$ and $l = 3$ spherical harmonics. From Zener's model for the influence of long-wavelength thermal fluctuations of $\hat{\mathbf{M}}(\mathbf{r})$ on the temperature dependence of magnetic anisotropies,[3] we predict that the $l = 3$ terms give rise to an appreciable increase with temperature of the anisotropy ratio r.

---

[1] N. V. Volkenshtein, G. V. Fedorov, and V. P. Shirokovskii, Fiz. Metal. Metalloved. **11**, 152 (1961).

[2] C. Zeng, Y. Yao, Q. Niu, and H. H. Weitering, Phys. Rev. Lett. **96**, 037204 (2006).

[3] C. Zener, Phys. Rev. **96**, 1335 (1954).

Main Topic A3 Magnetism and Spintronics

Structural, thermodynamic, and electronic properties of plutonium oxides from first principles

Gérald Jomard[1], *Bernard Amadon*[1], *François Bottin*[1], *Marc Torrent*[1]

1. CEA, DAM-DIF, F91297 Arpajon, France

We report *ab initio* calculations of the structural, electronic, optical and thermodynamic properties of plutonium oxides (PuO_2 and β-Pu_2O_3) [1]. In order to describe the basic features of the electronic structure, a method suited to take into account strong local correlations has to be used. We apply the LDA/GGA+U approximations to these compounds and compare it to the calculations of Sun *et al* [2]. Whereas a good agreement is obtained for PuO_2, our LDA and LDA+U results differs strongly from this study in the case of Pu_2O_3. In particular, the effect of the Hubbard parameter U on the volume is qualitatively and quantitatively different. Moreover, thermodynamic quantities differ. We thus focus our study on Pu_2O_3 and emphasize the importance of a careful and systematic search of the ground state in LDA+U: In particular, different hints for the occupation matrices corresponding to the electronic configurations allowed by symmetry have to be tried. This procedure is absolutely necessary to find the absolute minimum of the energy. We thus recover for Pu_2O_3 a more physical behaviour coherent with calculations on other systems, such as cerium oxydes.

[1] Jomard, Amadon, Bottin, Torrent, Phys. Rev. B **78**, 075125 (2008)
[2] Sun, Zhang, Zhao, J. Chem. Phys **128** 084705 (2008)

Main Topic: A3 Magnetism and Spintronics

Maximally localized Wannier function within linear combination of pseudo-atomic orbital method: Implementation and applications to transition-metal-benzene complex

Hongming Weng[1], *Taisuke Ozaki*[1], *Kiyoyuki Terakura*[1]

1. Research Center for Integrated Science (RCIS), Japan Advanced Institute of Science and Technology (JAIST), Nomi, Ishikawa 923-1292, Japan

Construction of maximally localized Wannier functions (MLWFs) has been implemented within the linear combination of pseudo-atomic orbital (LCPAO) method in software package OpenMX. The implementation is demonstrated to be applicable to both solid and molecular system no matter whether it is semiconducting or metallic. Detailed analysis is applied to three closely related materials, single benzene (Bz) molecule, organometallic Vanadium-Bz sandwich-like structural infinite chain, and $\mathrm{V}_n\mathrm{Bz}_{n+1}$ sandwich clusters. For Bz molecule, the obtained MLWFs are six p_z like orbitals near each carbon atom. The hopping integrals among these p_z orbitals decay quickly and can be used for tight-binding calculation. Using different initial guesses for the target WFs, two sets of physically reasonable WFs can be obtained for V-Bz infinite chain. In addition to five d orbital like WFs on V atom, the others can be six p_z like orbitals or six molecular orbitals of Bz. Though the latter set is a local minima of spreads function, the converged WFs are real and localized. The hopping integrals among these two sets of WFs are found to be nearly equivalent and suitable for tight-binding calculations. The on-site Coulomb interaction U is found to have little effect on the inter-site hopping integrals. In $\mathrm{V}_n\mathrm{Bz}_{n+1}$ case, the mechanism of ferromagnetic (FM) stability is reexamined within the space constituted by MLWFs and an important role played by middle Bz is newly revealed. It is shown that the on-site energy of pδ states from middle Bz is lower than those from edge Bz, which further reduces the FM stability.

Main Topic: A3: Magnetism and Spintronics

Magnetism and electron transport in metal decorated carbon nanotubes

Zeila Zanolli and *Jean-Christophe Charlier*

Université Catholique de Louvain, Unité de PCPM
European Theoretical Spectroscopy Facility (ETSF)
Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium
Zeila.Zanolli@uclouvain.be

First principles Density Functional Theory (DFT) and Non Equilibrium Green's Function (NEGF) methods have been used to investigate the magnetic and electronic transport properties of carbon nanotubes (CNTs) decorated with metallic nanoclusters.

Metallic CNTs can be thought as one-dimensional conductors and, as such, offer the opportunity of studying fundamental issues in electronic transport at the nanoscale. Metallic nanoclusters exhibit peculiar structural, electronic, and magnetic properties due to their finite size. In particular, small clusters of magnetic (as, for instance, Ni [1]) and non magnetic (as Au [2]) elements can have a net magnetic moment whose magnitude depends on the cluster size. Hence, decorating carbon nanotubes with nanometer-size metallic clusters can lead to nanomaterials with interesting magnetic properties. We present here the results of this theoretical study.

Metal decorated CNTs have been recently fabricated [3] and call for a theoretical investigation to unveil their fundamental properties and investigate possible applications in spintronic devices as nanomaterials with magnetic properties tunable with the cluster size.

This work is supported by the project "Nano2Hybrids" (EC-STREP-033311).

[1] S. E. Apsel *et al.*, Phys, Rev. Lett. **76**, 1441 (1996)
[2] Y. Yamamoto and H. Hori, Rev. Adv. Mater. Sci. **12**, 23 (2006)
[3] C. Bittencourt *et al*, Surf. Science, **601**, 2800 (2007)

Main Topic: A3 Magnetism and Spintronics

Influence of interface atomic structure on the magnetic and electronic properties of $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3(001)$ heterojunctions

Bing Zheng[1,2,3], *Nadia Binggeli*[1,4]

1. Abdus Salam International Centre for Theoretical Physics, Trieste 34014, Italy
2. Sincrotrone Trieste, Area Science Park, 34012 Basovizza, Trieste, Italy
3. Department of Materials Science and Engineering, Jilin University, Changchun 130021, China
4. Democritos National Simulation Center, INFM-CNR, Trieste I-34014, Italy

We have investigated, by means of *ab initio* pseudopotential calculations, the magnetic and electronic properties of abrupt $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3(001)$ heterojunctions, considering both TiO_2- and SrO- layer-terminations of $SrTiO_3(001)$ at the interface. The calculations were performed within the GGA + U approach, including structural relaxation. Contrary to the results of previous self-interaction-correction (SIC) linear-muffin-tin-orbital (LMTO) calculations, neglecting lattice relaxation, we find that both interface terminations lead to a ferromagnetic coupling between interfacial and bulk Mn atoms in $La_{2/3}Sr_{1/3}MnO_3$. The result questions a previous interpretation of the dead interface magnetic layers, observed experimentally in $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3(001)$ junctions, based on the antiferromagnetic coupling inferred from the SIC-LMTO calculations for the SrO-terminated interface. The presence of dead magnetic layers may therefore have a more extrinsic, defect-related origin. Our results also indicate that the interface termination has a significant impact on the Schottky barrier height and on the presence of localized interface states in the junction. The calculated n-type Schottky barrier height changes from 2.4 eV for the SrO terminated interface to 0.5 eV for the TiO_2 terminated interface, consistent with the available experimental values of $0.5 \sim 0.7$ eV for the TiO_2-terminated junction. At the abrupt SrO-terminated interface, we find that no intrinsic minority-spin localized interface states are induced near the Fermi energy, whereas minority-spin localized Ti-$3d$ t_{2g} interface states are present near the Fermi level at the TiO_2-terminated interface.

Main Topic: A5 Functional materials

Coexistence of tetrahedral and octahedral-like sites in amorphous phase change materials

S. Caravati[1,2], *M. Bernasconi*[1], *T. D. Kuehne*[2], *M. Krack*[2,3], *and M. Parrinello*[2]

1. Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, I-20125, Milano, Italy
2. Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, USI Campus, Via Giuseppe Buffi 13, 6900 Lugano, Switzerland
3. Paul Scherrer Institut, 5232 Villigen, Switzerland

Optical recording (DVD) and electronic non-volatile memories of new concept rely on the fast and reversible amorphous-to-crystal phase change of chalcogenide alloys. In spite of the great technological importance of these materials, the atomistic details of the phase change and of the amorphous structure are still matter of debate. Based on first principles molecular dynamics, we provide insight into the structure of amorphous $Ge_2Sb_2Te_5$ (GST), the material of choice for non-volatile memory applications. Simulations reveal that the amorphous phase, quenched from the melt, displays two types of short range order: a tetrahedral geometry for nearly half of the Ge atoms and a defective octahedral-like environment of the other Ge, Sb and Te atoms. The tetrahedral geometry is peculiar of the amorphous, while the defective octahedral-like geometry recall the structure of crystalline GST. The coexistence of the two types of local environments is the key to understand the two apparently contradictory and peculiar features of GST exploited in the devices, namely the strong optical and electronic contrast between the amorphous and crystalline structures and the high speed of the phase change. Results on GeSbTe materials at different compositions and/or doped with isovalent atoms will be presented as well.

P 00100

Main Topic: A5 Functional Materials

Boron and boron carbides from first principles

Emmanuel Betranhandy[1], *Nathalie Vast*[1], *Jelena Sjakste*[1]

1. Laboratoire des Solides Irradiées, CEA-Direction des sciences de la matière - CNRS - Ecole Polytechnique, 91128 Palaiseau, France

In this work, we focus on the understanding gained from the investigation of the physical properties of boron and boron-carbides[1, 2, 3] with theoretical methods based on density functional theory (DFT)[4]. Together with the examination of the DFT total energies of various atomic configurations in the unit cell[3, 5, 6], comparisons between the experiments of the theoretical vibrational[3] or NMR[6] spectra led to determinate the atomic structure of B_4C as C-B-C chains linking mostly $B_{11}C$ icosahedra, and a few percent of $B_{10}C_2$ icosahedra. In this work we find that at lower carbon concentration all models are metastable with respect to B_4C plus □-boron[7, 8]. This could explain actual difficulties in the synthesis of clean samples. Furthermore we discuss effects of temperature and/or pressure on stabilities and properties. Finally, the idea of combining high hardness and superconductivity in the same material by doping boron-rich solids has emerged[4, 9, 10]. We show results on the strength of the electron-phonon coupling constant obtained with DFT-based methods in $B_{13}C_2$.

Acknowledgements

Support from DGA through a grant is gratefully acknowledged. Results have been obtained in part with the espresso package[11, 12] and computer time granted by CEA – DSM on the NEC SX8.

1. N. Vast, S. Baroni, G. Zérah, J.M. Besson, A. Polian, M. Grimsditch and J.C. Chervin, Phys. Rev. Lett. **78**, 693 (1997).
2. R. Lazzari, N. Vast, J.M. Besson, S. Baroni and A. Dal Corso, Phys. Rev. Lett. **83**, 3230 (1999); Ibid **85**, 4194 (2000).
3. M. Calandra, N. Vast and F. Mauri, Phys. Rev. B **69**, 224505 (2004).
4. http://nobelprize.org/nobel_prizes/chemistry/laureates/1998/kohn-lecture.html
5. D. Bylander, L. Kleinman, and S. Lee, Phys. Rev. B **42**, 1394 (1990).
6. F. Mauri, N. Vast and C.J. Pickard, Phys. Rev. Lett. **87**, 085506 (2001).
7. Unpublished results obtained with J. Sjakste.
8. J. Saal, S. Shang and Z.-H. Liu, Appl. Phys. Lett. **91,** 231915 (2007).
9. S. Gunji and H. Kakimura, Phys. Rev. B **54**, 13665 (1996).
10. H. Dekura, K. Shirai and H. Katayama-Yoshida, J. Phys. : Cond. Matter **19**, 365241 (2007).
11. S. Baroni, S. de Gironcoli, A.D. Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
12. http://www.pwscf.org

Main Topic: A5 Functional Materials

First Principles Study of the Oxide at Ge-GeO_2 Interfaces

Jan Felix Binder, Peter Broqvist, and Alfredo Pasquarello

Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Theoretical Physics, CH-1015, Switzerland
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015, Switzerland

As Si-based metal-oxide-semiconductor devices are approaching their technological and physical limits due to aggressive scaling, the search for new material solutions intensifies. Germanium shows high electron and hole mobilities together with a small electronic band gap, and is seriously being considered as a viable alternative to silicon. However, current state-of-the-art germanium/insulator interfaces show excessively high defect densities compared to conventional silicon/insulator interfaces. In this context, the characterization of both the structural and electronic properties of the Ge/GeO_2 interface is highly relevant. Using a density functional approach, we study the electronic and structural properties of the oxide in the vicinity of the Ge-GeO_2 interface. For this purpose, we considered various structural models of GeO_x, in which x varies between $x = 0$ (Ge) and $x = 2$ (GeO_2). Our set of models comprises both crystalline and amorphous structures. The crystalline models include beta-crystabalite-like structures for GeO_x and alpha-quartz-like structures for GeO_2. We obtained amorphous models of GeO_2 and GeO through an *ab initio* molecular dynamics quench from the melt. We then addressed the band alignment at the Ge-GeO_2 interface by adapting a model structure of the Si-SiO_2 interface. The band offsets are obtained through the application of an alignment scheme based on hybrid density functionals which reproduces the experimental band gaps of the interface components. The calculated valence band offset of 3.7 eV favors the low-energy side of the range of measured offsets (3.6–4.5 eV).

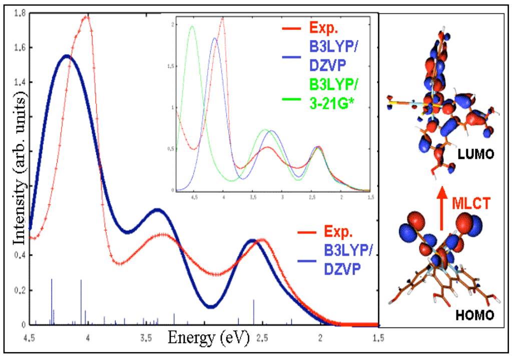
Main Topic: A5 Functional Materials

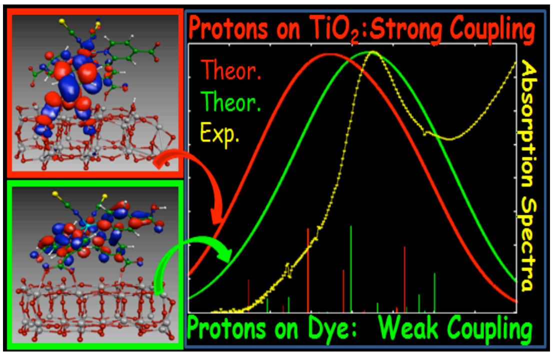
Ab initio modeling of nanoscale materials and devices

Filippo De Angelis[1]

1. Istituto di Scienze e Tecnologie Molecolari (ISTM-CNR) and Dipartimento di Chimica, Università di Perugia, 06123, Perugia, Italy. E-mail:filippo@thch.unipg.it

We present the potential of computer simulation by *ab initio* methods applied to the investigation of the structural, electronic and spectroscopic properties of Ru(II)-dyes and nanoscale systems of interest in the field of Dye-Sensitized Solar Cells and OLEDs. We devised over time a computational strategy based on DFT TD-DFT which allows the accurate calculation of excited state properties of large systems in solution. The main ingredients of our computational strategy are discussed. In particular, our efficient implementation of the Car-Parrinello method allows us to calculate the structures and dynamics of realistic systems; and the inclusion of solvation effects provides a direct connection of the calculated properties to the experimental quantities. Due to these methodological advances, theory is today a predictive tool, allowing us to scrutinize the properties of several organic and inorganic systems before their synthesis. A computational tool for the *in silico* screening of dye-sensitizers is therefore presented. We then present realistic models of DSSC devices, obtained by adsorbing dyes on TiO_2 nanoparticles, simulating the fundamental processes of light-harvesting and charge injection in DSSCs. Modelling of the optical properties of ZnO nanostructures in relation to DSSCs applications will also be presented.





[1] P. Giannozzi, F. De Angelis, R. Car *J. Chem. Phys.* **2004**, *120*, 5903.
[2] S. Fantacci, F. De Angelis, A. Selloni. *J. Am. Chem. Soc.* **2003**, *125*, 4381.
[3] F. De Angelis, S. Fantacci, M. Grätzel et al. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
[4] J-H. Yum, F. De Angelis, M. Grätzel et al. *J. Am. Chem. Soc.* **2007**, *129,* 10320.
[5] F. De Angelis, A. Tilocca, A. Selloni *J. Am. Chem. Soc.* **2004**, *126*, 15024.
[6] F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel et al. *Nano Lett.* **2007**, *7,* 3189.
[7] F. De Angelis, S. Fantacci, M. Grätzel et al. *J .Am. Chem. Soc.* **2007**, *129,* 14156.
[8] D. P. Hagberg, F. De Angelis, M. Grätzel et al. *J .Am. Chem. Soc.* **2008**, *130,* 6259.

Main Topic: A5 Functional Materials

An epitaxial new phase of HfO_2 for ultrascaled devices

A. Debernardi[1], *C. Wiemer*[1], *M. Fanciulli*[1,2]

1. MDM National Laboratory, CNR-INFM, Via C. Olivetti 2, 20041 Agrate Brianza (MI), Italy
2. Dipartimento di Scienza dei Materiali, Universitá di Milano Bicocca, Milano, Italy

Due to the large mismatch between the oxide and the semiconductor, the unexpected preferential orientation of monoclinic high dielectric constant oxides on Ge and GaAs (001) high-mobility substrates has puzzled up to now material scientists interested in a defect-free interface for nano-electronic applications. By state-of-the-art first principle calculations we identify the microscopic mechanism responsible for the oriented growth of HfO_2 on germanium (001) surface. The preferential orientation of the monoclinic structure is related to the relaxation of the epitaxially stabilized anatase phase when a critical thickness is reached.[1] In fact, the preferential orientation of the monoclinic structure follows the inplane axis of the anatase phase, as proven by accurate X-ray scattering measurements.[1] According to first principles simulations, the anatase phase is almost lattice matched with the substrate allowing to control at the atomic level its interface with the semiconductor. Further, the high-dielectric constant and the band offset with the substrate computed for the anatase phase - that are comparable with the values obtained for bulk monoclinic phase taken from literature- make anatase HfO_2 a promising candidate for the integration of high-κ dielectrics in future complementary-metal-oxide-semiconductor devices.

[1] A.Debernardi, C.Wiemer, M.Fanciulli ”Epitaxial phase of hafnium dioxide for ultra-scaled electronics”, Phys. Rev. B., Vol. 76, 155405 (2007).

Main Topic: A5 Functional Materials

Efficient coupling in organic-inorganic systems: a theoretical study

G. Mattioli[1,2]**,** *F.Filippone*[1]**,** *Paola Alippi*[1]**,** *P. Giannozzi,*[3] *and A. Amore Bonapasta*[1]

1. *Istituto di Struttura della Materia (ISM) - CNR, Via Salaria Km. 29.5, CP 10, 00016 Monterotondo Stazione, Italy*
2. *Dipartimento di Chimica, Università di Roma La Sapienza, P.le A.Moro 2, 00185 Roma, Italy*
3. *Dip. di Fisica, Università di Udine and Democritos Natl. Simulation Center, via delle Scienze 208, 33100 Udine, Italy*

Hybrid materials containing both inorganic and organic components may give rise to novel properties if a strong organic-inorganic coupling is achieved.[1] An example is offered by metallo-organic macrocyclic complexes (MOMC) interacting with inorganic semiconductors. MOMC are characterized by a macrocycle carrying a metal (or a group containing a metal) in its center and include Phthalocyanines (Pcs), metalloporphyrins and related biological molecules.[1,2] These MOMC feature a large hyperpolarizability of π-electron clouds of the macrocycle which accounts for the peculiar transport and nonlinear optical properties (NLO) shown by these molecules (Fig. 1).

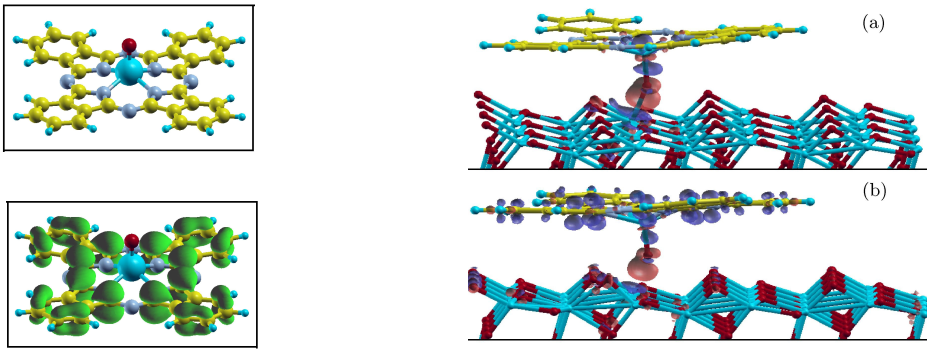


Fig.1 Left panel: structure (top) and electron density map of the π-electron clouds (bottom) for a OTiPc molecule. Right panel: structure and difference electron density maps for a OTiPc/TiO2 system; (a) undoped TiO2, (b) *p*-type doped TiO2. Red (blue) surfaces cover areas where the difference is positive (negative). O, Ti, N, C, and H atoms are represented by the red, blue, gray, yellow, and small blue spheres, respectively.

In a Pc-semiconductor *heterostructured junction*, a tuning of the NLO properties of the organic film driven by the interaction with the inorganic substrate could be used to design quite new opto-electronic devices. Unfortunately, a very weak coupling generally characterizes the interaction of Pcs with semiconductor substrates, although stronger coupling (chemical binding) was recently observed in ordered monolayers of different Pcs deposited on In-rich InAs and InSb surfaces.[3] These results point to the general and fundamental problem of how to achieve an efficient organic-inorganic coupling, thus opening the road towards novel materials. Previously[4] we performed a DFT study of the organic-inorganic interaction in a few MOMC-semiconductor systems, assuming that *two main conditions* have to be both satisfied to achieve an efficient coupling: i) the formation of appreciable surface-molecule chemical bonds, and ii) a molecule-surface charge transfer involving the π-electron clouds responsible of the Pc NLO and transport properties. Here, we extend that study to further Pc-semiconductor systems. Present results clarify the surface-molecule charge-transfer mechanisms as well as the conditions favoring an efficient coupling. In particular, regarding a surface-molecule charge-transfer, they show that the typical donor behavior of the Pc molecules can be reversed by substituting peripheral H atoms of the macrocycle with electron-acceptor functional groups. This result contributes to state a general procedure for the theoretical design of efficiently coupled molecule-semiconductor systems appropriate for a wide class of MOMC and, then, of hybrid heterostructures.

[1] A. K. Chetham and C.N. R. Rao, Science, **318**, 58 (2007); H. Wende *et al.*, Nature Mater., **6**, 516 (2007).

[2] S. R. Forrest, Chem. Rev., **97**, 1793 (1997); G. De la Torre *et al.*, Chem. Rev., **104**, 3723 (2004).

[3] N. Papageorgiou *et al.*, Progress in Surface Science, **77**, 139 (2004).

[4] G. Mattioli *et al.*, Phys. Rev. Lett., **101**, 126805 (2008).

P 00105

Main Topic : A5 Functional Materials

Structural and Electronic Properties of SmSe and SmTe under Compression

Dinesh C. Gupta and Subhra Kulshrestha

Condensed Matter Theory Group, School of Studies in Physics, Jiwaji University,
Gwalior – 474 011 (M.P.), INDIA

Email : sosfizix@yahoo.co.in

ab-initio pseudo-potential calculations within the framework of density functional theory have been used to investigate the structural and electronic properties of SmSe and SmTe in its stable (NaCl-B1) and high-pressure (CsCl-B2) phases. In this approach, we have used the spin polarized GGA based on exchange-correlation energy optimization for calculating the total energy using SIESTA code. The magnetic phase stability was determined from the total energy calculations for both the nonmagnetic (NM) and magnetic (M) phases. These theoretical calculations clearly indicate that at ambient and high pressures, the magnetic phase is more stable than the non magnetic phase. Also, the Sm ion is described with either five or six localized *f* electrons. Under compression the Sm chalcogenides undergo first order transitions from Sm^{2+} to Sm^{3+} with the delocalization of f^6 electrons into 5*d* states of Sm followed by a structural transition from B1 to B2 phase. The first-principles studies on the Sm^{2+} to Sm^{3+} and B1□B2 structural phase transformation for both the compounds along with their electronic properties have been carried out. The structural properties viz, equilibrium lattice constant, bulk modulus, its pressure derivative, transition pressure and volume collapse agree well with the experimental results. The spin-polarized GGA calculations of electronic structure show the stable solution of SmSe and SmTe is a metal. The metallic nature may be attributed to the spin-orbit splitting between $4f^{5/2}$ and $4f^{7/2}$ states. At normal volume, these two sets of bands are crossed by the lowest 5*d* band resulting in a metallic behavior. The metallic behavior of these compounds at ambient conditions follows the general trend that LSDA and GGA are not capable of correctly predicting the semiconducting ground state of the highly correlated electron systems. This limitation of the present calculations may be overcome by LSDA+U (onsite Coulomb interaction).

Main Topic: A5 Functional Materials

Towards to understanding the role of the metal – ligand bond strength in the stability of metal – organic frameworks (MOF)

A. Rabdel Ruiz-Salvador[1] , *Ariel Gomez* [2], *L. Marleny Rodriguez-Albelo*[1],
Mario Basterrechea-Rey[3], *Dewi W. Lewis*[4]

1. Zeolites Engineering Laboratory, Institute of Science and Technology of Materials (IMRE), University of Havana, 10400 Havana, Cuba.
2. Department of Physiscs, University of Guelph, Guelp, Ontario, Canada.
3. Department of Organic Chemistry, Faculty of Chemistry, University of Havana, 10400 Havana, Cuba
4. Chemistry Department, University College London, 20 Gordon St., London, UK WC1H 0AJ

Metal – Organic Frameworks (MOF) are an emerging class of nanoporous materials that have attracted large attention due to their novel and interesting properties that support applications like catalysis, gas adsorption and storage, molecular separations, electronic and magnetic devices, etc [1]. Despite of a large set of crystallographic and theoretical studies that have been already performed on these materials, today is still unclear the role of the metal – ligand role in the topology and stability of different frameworks. In order to deepen in this regards, we have constructed two families (Zn an Cd based) of hypothetical MOFs by using of the newly developed automatic structure building method TOBUNPOROUS (TOpological BUlding of NanoPOROUs Solids) [2]. The energy of the solids has been calculated by DFT using PEB functional and numerical basis sets. A good correlation has been found between the topological density and the energy of the cell. The calculations shown little but noticeable differences of the behavior of both families, which has allowed to learn more about the role of the overall ionicity of the solids and in particular the effect in changing the strength of the metal – ligand on favoring the formation of a number of frameworks [3]. The discussion is also directed towards the comparison between the energetic relation of these hypothetical MOFs and the analogous framework topology zeolites.

1.- G. Ferey, Stud. Surf. Sci Catal, Vol 170 (2007) 66.
2.- A. R. Ruiz-Salvador, A. Gomez, L. M. Rodriguez-Albelo, M. J. Basterrechea-Rey, and D. W. Lewis, submitted.
3.- A. R. Ruiz-Salvador, A. Gomez, L. M. Rodriguez-Albelo, M. J. Basterrechea-Rey, and D. W. Lewis, in preparation.

Main Topic: A5 Functional Materials

A comparative investigation of H_2 interaction in Cd- and Zn-based MOF-5: A density functional theory based study

P. Srepusharawoot[1,2], C. Moyses Araujo[1], A. Blomqvist[1], R. H. Scheicher[1]
and R. Ahuja[1,3]

[1]Condensed Matter Theory Group, Department of Physics and Materials Science, Box 530, Uppsala University, SE-751 21 Uppsala, Sweden
[2]Department of Physics, Faculty of Science, Khon Kaen University, 40002 Khon Kaen, Thailand
[3]Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden

Abstract

Hydrogen physisorption energies at all possible adsorption sites near metal oxide cluster in Cd- and Zn- based Metal Organic Framework-5 (MOF-5) were intensively studied by using density functional theory. Out of three different exchange-correlation functionals, namely Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) with Perdew-Wang 91 and Perdew, Burke and Ernzerhof functionals are employed in this study. Our results reveal that the LDA yields a qualitatively correct description of the H_2 adsorption energy trend in Zn- based MOF-5. In addition, the binding energies for all adsorption sites in Cd- and Zn- based MOF-5 are seen to be of the same order of magnitude, but with a generally stronger binding in Cd-based MOF-5 as compared to Zn- based MOF-5. The hydrogen adsorption energy at secondary adsorption sites is increased by about 25 % compared to the Zn- based MOF-5. This result implies that Cd- based MOF-5 would be better suited to store hydrogen at higher temperatures than Zn- based MOF-5.

Main Topic: A5 Functional Materials

Electronic structure induced reconstruction and magnetic ordering at the $LaAlO_3|SrTiO_3$ interface

Zhicheng Zhong and P. J. Kelly

CMS,Faculty of Science and Technology and MESA+ Institute for Nanotechnology,
University of Twente
Z.C.Zhong@utwente.nl

Using local density approximation (LDA) calculations we predict $GdFeO_3$-like rotation of TiO_6 octahedra at the n-type interface between $LaAlO_3$ and $SrTiO_3$. The distortion is crucial to the formation of a charge-ordered (CO) antiferromagnetic insulating (AFMI) ground state and other charge, magnetic and orbital properties, and results in a characteristic buckling of the Ti-O-Ti bonding at the interface.

P 00109

Main Topic: A5 Functional Materials

Phase diagram of FeAs-based superconductors: searching for a higher T_c

Zhicheng Zhong, Qinfang Zhang, Pengxiang Xu and P. J. Kelly

CMS,Faculty of Science and Technology and MESA+ Institute for Nanotechnology,
University of Twente
Z.C.Zhong@utwente.nl

Using first principles calculations, we study the magnetic phase diagram of the newly discovered high temperature $Re(O_{1-x}F_x)FeAs$ superconductor (Re=La--Dy), as a function of doping, of the FeAs in-plane lattice constant a and of the distance between the Fe and As planes. Compared with recent experimental data for different doping, external pressure or chemical substitution, the phase diagram is qualitatively consistent with most experimental findings. The existence of a tricritical point (TCP) in the phase diagram suggests new ways of enhancing T_c for iron-pnictide based superconductors.

Main Topic: A6 Surfaces

Single alkali adatoms on Cu(111) surface: role of surface band structure

S. Achilli, *M.I. Trioni*,

CNISM and Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,
Via Cozzi 53, 20125 Milano, Italy

Alkali adatoms on metal surface have been extensively studied in the past decades as prototype of simple adsorbed system. In spite of their supposed simplicity they showed a variety of phenomena ranging from quantum well states, surface resonances, and a not trivial scenario of empty states. In this respect, recent two-photon photoemission spectra have shown that a sharp empty state is present around 1.7 eV above the Fermi level for all the alkali adatoms adsorbed on Cu(111) at very low coverage. In this work we present a new way to model the single adsorbate on an extended metal surface in the DFT ab-initio framework which is able to account for the experimental evidences. The key ingredients of such an approach are the presence of a semiinfinite substrate with its realistic surface band structure together with the presence of an isolated adatom. This can be carried out using a 1-D modulated potential for the surface, as proposed by E.V. Chulkov, and the "embedding approach" for single adsorbate. Results for all the alkali adatoms will be presented and compared with experimental two-photo photoemission spectra. The simpler "adatom on jellium" case and the more complex "dilute overlayer on periodic substrate" case will be critically analyzed in comparison with the presented approach.

Main Topic: A6 Surfaces.

Band-alignment issues in the first-principles simulations of ferroelectric nanocapacitors.

Pablo Aguado-Puente and Javier Junquera
CITIMAC, Universidad de Cantabria, Avda. de los Castros s/n, E-39005 Santander, Spain

Massimiliano Stengel and Nicola A. Spaldin
Materials Department, University of California Santa Barbara, CA 93106-5050, USA

Ferroelectric oxide nanostructures have been a very attractive research topic in the last few years [1, 2]. The combination of theoretical methods with recent advances in ultrathin film growth and characterization techniques have led to the discovery of new phenomena in the nanoscale regime, and have opened the door to the design of oxide nanostructures with new and promising fuctionalities. First-principles simulations are playing an important role in this new research avenue, allowing to ascertain the behaviour of interfaces between different materials, and to gauge the relative influence of the different boundary conditions [3] and the interfacial chemistry [4]. In the theoretical description of the interfaces, the distortions of the crystalline cells, the atomic displacements, the electronic structure, and, in particular, the band gap have to be accurately described simultaneously [5].

It is well known that the LDA and GGA usually lead to a significant understimation of the band gaps of the Kohn-Sham electronic band-structure. This DFT bandgap underestimate prevents accurate predictions of the barriers simultaneously for electrons and holes in metal/ferroelectric interfaces and can, in many cases, produce pathological situations where the Fermi level of the metal is erroneously aligned with the conduction bands of the ferroelectric producing unphysical population of the conduction bands of the ferroelectric. In this poster, analyzing the Projected Density Of States (PDOS) and the Local Density Of States (LDOS) around the Fermi energy, we discuss some of the fingerprints of selected pathological cases, both in unpolarized capacitors (where the ferroelectric material is in a centrosymmetric configuration), and in a polar capacitor where the underestimate of the electron barrier artificially lowers the breakdown field.

---

[1] M. Dawber, K. M. Rabe, and J. F. Scott, Rev. Mod. Phys. **77**, 1083 (2005).

[2] Ph. Ghosez and J. Junquera, *Handbook of theoretical and computational nanotechnology* (American Scientific Publishers, Stevenson Ranch, CA, 2006), vol. 9, pp. 623–728.

[3] J. Junquera and Ph. Ghosez, Journal of Computational and Theoretical Nanoscience **77**, 165107 (2008).

[4] M. Stengel, D. Vanderbilt, and N. A. Spaldin, arXiv:0811.0632

[5] D. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Íñiguez, and Ph. Ghosez, Phys. Rev. B **77**, 165107 (2008).

Main Topic: Applications: A6 Surfaces

Beryllium – tungsten interaction: formation of alloys at the interface

A.Allouche
Physique des Interactions Ioniques et Moléculaires,
CNRS and Université de Provence,
Campus Scientifique de Saint Jérôme, service 242, 13397 Marseille Cedex 20 - FRANCE

Beryllium, tungsten and carbon are planned as wall materials for the future international tokamak (ITER). Be and W will be the dominant components and therefore the formation of binary Be-W alloys under plasma action is one of the most important issues in plasma-wall interaction processes at the first wall.

The formation of alloys and their reactivity under physical sputtering and chemical erosion constitute a new challenge for solid states physics and chemical reactivity. The laboratory experiments show that annealing of a tungsten film on a beryllium sample leads to formation of a several nm thick Be/W alloy film. The inverse experiment is more difficult and the alloy film is not stable. This communication proposes a theoretical study of the first steps of the formation of these alloys based on the first principles DFT method. For each calculation the electronic structure of the formed compound is analyzed through density of states (DOS) calculation and we show that the substrate surface relaxation has a predominant influence on the electronic energy levels distribution and makes the reaction feasible or not.

Main Topic: A6 Surfaces

Benchmarking DFT surface energies with Quantum Monte Carlo

S.J. Binnie[1,2,3], *D. Alfè*[1,2,3,4], *M.J. Gillan*[1,2,3]

1. Materials Simulation Laboratory, University College London, Gower Street, London, WC1E 6BT, UK
2. Dept. of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK
3. London Centre for Nanotechnology, University College London, Gower Street, London, WC1H 0AH, UK
4. Dept. of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, UK

Previous work has demonstrated that for many materials, surface energies σ calculated by Density Functional Theory (DFT) methods appear to vary significantly depending on the exchange correlation (xc) functional used. This could pose significant problems when using DFT for predicting structures of nanocrystals both in vacuum and on substrates. Here we present initial results from a systematic study of σ for several ionic solids (LiH, LiF, NaF) using the VASP code and its projector augmented wave implementation of DFT. Calculations were performed using the four of the functionals available in VASP (LDA, PW91, PBE and RPBE) along with the recent Wu and Cohen modification of PBE. The results we present show that there is indeed a significant variation in σ due to differing functionals. Furthermore we are able to ascertain which functionals gave the most accurate results by performing calculations of σ for LiH using diffusion quantum Monte Carlo methods which are generally accepted to be significantly more accurate, albeit more expensive, in calculating these quantities.

Main Topic: A6 Surfaces

Diffusion of H and Si on Si(110)

V. Brázdová[1,2], *D. R. Bowler*[1,2,3]

1. London Centre for Nanotechnology, UCL, London WC1H 0AH, UK
2. Materials Simulation Laborator, UCL, Gower St, London WC1E 6BT, UK
3. Dept. of Physics & Astronomy, UCL, Gower St, London WC1E 6BT, UK

Silicon has been immensely important in condensed matter physics, surface science and industrial applications. The Si(001) and Si(111) surfaces have been intensively studied, and the elucidation of their complex reconstructions has advanced the study of their surface properties. Si(110) has been less intensively studied, but also shows interesting scientific and technological properties. First, it exhibits a complex stepped (16×2) reconstruction, whose atomic structure is still not fully understood (proposed structures do not fit all available experimental data). Second, recent developments in CMOS transistor technology (e.g. FinFETs[1] and structures grown by patterned ALE[2]) are either grown on or create Si(110) surfaces. The growth process involves gas sources which will leave hydrogen and possibly silicon on the sidewalls, and understanding how these species diffuse on Si(110) is vital to controlling growth.

We will present results of comprehensive modelling studies on the diffusion of Si and H adatoms on Si(110)-(1×1). These are a necessary starting point for understanding the growth of features with (110) sidewalls; the Si adatom diffusion will also feed into the studies of Si(110)-(16×2), as the formation of this reconstruction seems to involve significant amounts of mass transport. Barriers and structures resulting from diffusion will be presented, and their implications for growth and reconstruction will be discussed.

References

[1] Mizuno, T.; Sugiyama, N.; Tezuka, T.; Moriyama, Y.; Nakaharai, S.; Takagi, S. *IEEE Trans. Electron Devices* **2005**, *52*, 367.

[2] Suda, Y.; Hosoya, N.; Miki, K. *Appl. Surf. Sci.* **2003**, *216*, 424–430.

Bonding of graphene on Ir(111) surface

Radovan Brako[1], *Damir Šokčević*[1], *Predrag Lazić*[2]

1. R. Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia
2. Institut für Festkörperforschung(IFF), Forschungszentrum Jülich, 52425 Jülich, Germany

Graphene, a two dimensional honeycomb structure of strongly bound carbon atoms, has attracted a lot of attention recently due to its electronic properties, both as a fundamental challenge and as a promising material for novel electronic devices. Graphene is the building block of graphite, which has been used to exfoliate single or multiple layers onto insulating substrates. Graphene layers have also been prepared on SiC and metals by various growth techniques. The usual Density Functional Theory (DFT) calculations nicely describe the strong sp^2 carbon bonds of the honeycomb structure, but either overestimate the binding of a graphene layer with the substrate (LDA) or seriously underestimate it (GGA). The reason is the lack of the proper description of the non-local corellation effects which lead to the van der Waals interaction. We have performed calculations of the structure of graphene in multilayer configurations and as an overlayer on Ir(111), by complementing the DFT calculations with the recently developed approach which takes into account the long-range correlation effects in a seamless manner. Particularly interesting is the case of Ir-graphene-Ir sandwiches, which have recently been observed experimentally in the form of a regular array of iridium clusters on top of graphene adsorbed on Ir(111) surface. Our calculations show that carbon atoms change to sp^3 electronic configuration in such places, with characteristic buckling of the honeycomb lattice and lenthening of the C–C bond. We discuss the weaknesses and strengths of various DFT approaches, the standard LDA, GGA, and GGA complemented with the nonlocal correlation in a post-processing procedure. Our results give clear insight on how to treat theoretically the interaction of graphene sheets with substrates.

Main Topic: A6 Surfaces

Ab initio simulations of Protein Surface Interactions mediated by Water

Arrigo Calzolari[1], *Stefano Corni*[1], *Rosa Di Felice*[1], *Giancarlo Cicero*[2], *and Alessandra Catellani*[3,1]

1. CNR-INFM National Center on nanoStructures and bioSystems at Surfaces (S3), Modena Italy
2. Polytechnic of Torino, Department of Physics, 10129, Torino, Italy
3. CNR-IMEM, Parco Area delle Scienze, 37A, I-43100 Parma, Italy

Recent combinatorial biotechnologies have shown that the molecular recognition capability of proteins can be specifically oriented toward inorganic surfaces. However, at present the principles regulating protein-surface interactions are poorly understood. In addition, the exact role of the water molecules belonging to the protein solvation shell in the process of protein-surface interaction is unknown. The comprehension of the microscopic mechanisms that regulate protein-surface interaction, and the description of the protein hydration layer structure close to the surface would foster several technological applications, ranging from biomaterials to nanobioelectronics.

In order to address some of the afore mentioned problems, we present a first-principles description of the interaction between a prototype protein molecule (serin-based beta-sheet) and a gold surface, by explicitly taking into account the hydration layer in a liquid environment surrounding the molecule and the surface. In particular, we perform extensive (several ps) ab initio molecular dynamics (Car-Parrinello) simulations at finite temperature, using plane-wave Density Functional Theory. Our results on the microscopic structure of the hydration layer, and its modifications induced by confinement effects close to the gold surface unravel the role of the interfacial water in facilitating peptide adsorption.

A6 Surfaces and Interfaces

Atomic and electronic structure at hybrid metal/II-VI-semiconductor interfaces

R. de Paiva and R. Di Felice

National Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR,
Via Campi 213/A, 41100 Modena, Italy

Hybrid metal-semiconductor nanoparticles have attracted great interest due to their potential application in developing future electronic and optoelectronic nano-devices. The possibility to design the functionalities by tailoring shape and size, as well as to exploit the combination of properties from the semiconductor (electrical or optical) and from the metal (optical, electrical, chemical, connectivity), suggests many viable devices, including ultra-small transistors, memory elements, light-emitting elements and sensors. Despite this huge potential, most applications of nanoparticles have been limited so far to isotropic shapes, and metalsemiconductor nano-hybrids have been little investigated. These limitations were especially due to difficulties in their production. Recently, successful synthesis paradigms for semiconductor rods (mostly CdSe), and successively for Au/CdSe and Au/CdS nanodumbbells have been demonstrated. These experimental achievements have significantly driven efforts to characterize their optical and electrical performance, as well as to theoretically understand their properties. Besides the potential applications, the electronic properties of semiconductor nano-rods and hybrid metal-semiconductor nano-dumbbells are extremely interesting from a fundamental viewpoint, to investigate the mixing of electron states between two different materials in a size regime where quantization effects are expected to play a major role. In this context, we have carried out a plane-wave pseudopotential density functional theory study of Au thin films on CdSe(0001) and CdSe(0001) surfaces, with the aim to understand if atomic mixing between atoms of the overlayer and of the substrate occurs, how it is affected by different chemical environments, and what are the consequences of the mixing on the band-structure of the hybrid system. This is a first required step to unravel meta-stable interface geometries and mechanisms for electronic mixing that may occur also in confined nano-particles. We have considered several possible geometries. We present stability diagrams, densities of states, electron wave functions, work functions, and Schottky-barrier height. The analysis of the results reveals that stable Au bilayers may be formed on CdSe surfaces within the allowed range of Cd chemical potential and in Au-rich conditions [R. de Paiva and R. Di Felice, ACS Nano (2008), in press]. Significant orbital mixing between Se and Au occurs at the interface. Although current growth methods likely do not produce epitaxial structures, we believe that our results may on one hand give indications on how to stabilize very thin ordered layers that fix the kind of interface mixing, and on the other hand are anyway representative of qualitative features that occur upon metal-semiconductor electronic interaction.
Early results on Au/CdS interfaces show a quite similar behavior and quantitative differences.

Main Topic: A6 Surfaces

Spontaneous polarization of ZnO nanostructures

Giancarlo Cicero[1], *Andrea Ferretti*[2], *Alessandra Catellani*[3]

1. Material Science and Chemical Engineer Department, Politecnico of Torino, C.so Duca degli Abruzzi 24, I–10129 Torino, Italy.
2. Dipartimento di Fisica, Università di Modena e Reggio Emilia, and Natl. Center S3 of CNR-INFM, Via Campi 213/A, I–41100 Modena, Italy.
3. CNR-IMEM, Parco Area delle Scienze 37A, I–43100 Parma, Italy.

The advent of nanostructured devices critically enhances the role of surface and interface effects on bulk properties and determines the physical characteristics of the material: in particular, the understanding of the electronic properties of nanosized structures requires a proper accurate treatment. Here we report on first principles density functional calculations of the structural and electronic properties (including polarization) of ZnO nanowires grown along the [0001] direction with (1-100) exposed cuts, with a diameter range of about 9-23Å. We compare the results with those of (1-100) "non-polar" surface of hexagonal zinc oxide (ZnO). We discuss the changes in the nanostructures spontaneous polarization in terms of two contributions, one related to changes in equilibrium lattice parameters at the nanoscale and the other related to surface effects. We compare our results with those obtained for nanostructures based on materials with different polarity (e.g. SiC and InN).

Main Topic: A6 Surfaces

Stability and magnetism of hydrogen dimers on graphite

Yves Ferro, Sabine Morisset, Alain Allouche

Laboratoire de Physique des Interactions Ioniques et Moléculaires
Université de Provence /CNRS - UMR 6633, Campus de Saint Jérôme, Services 242
13397 Marseille Cedex 20, France

yves.ferro@univ-provence.fr
http://sites.univ-provence.fr/wpiim/themes/spectrom.htm

Molecular hydrogen recombination on graphitic surfaces is of crucial interest in material sciences, particularly in topics related to nuclear fusion or fuel-cells. H dimers are some key structures in the H desorption and/ or H recombination mechanisms on graphite. The enhance stability of some peculiar pairs of H atoms was previously shown experimentally and theoretically as well [1]. H dimers on graphite also exhibit various magnetic properties depending on the positions of the monomers.

We here report on the magnetism and stability of H dimers on a graphene sheet. The dimers investigated here are found to be in ferromagnetic, antiferromagnetic, or nonmagnetic states. Results obtained from DFT calculations [3] on the H dimer adsorption are analyzed with the help of spin-density maps. We thereby show that the dimer stability results from the magnetic properties of the pair of H atoms on graphene. The enhanced stability of dimers adsorbed in *ortho* and *para* positions is particularly emphasized and is a consequence of the formation of a π bond. This provides a rationalization of the H dimer stabilities and magnetic properties [4].

This comprehensive view eventually helps us to identify hydrogenated “star” structure observed on graphite using a STM technique by L. Hornekaert et al [5]. These structures are elucidated on the basis of our calculations. The origin of their stability is also understood.

[1] Hornekaert et al, Phys. Rev. Lett. 96 (2006) 156104.
[2] Rougeau et al, CPL 431 (2006) 135.
[3] http://www.pwscf.org
[4] Y. Ferro *et al.*, Phys. Rev. B, 78 (2008) 085417.
[5] L. Hornekært *et al.*, Chem. Phys. Lett. 446 (2007) 237.

Main Topic: A6 Surfaces

Optimal Strictly Localized Basis Sets for Noble Metal Surfaces

S. García-Gil[1], *A. García*[2], *N.Lorente*[1] ,*P.Ordejón*[1]

1. Centre d'Investigaciò en Nanociència I Nanotecnologia CIN2 (CSIC-ICN)
2. Institut de Ciència de Materials de Barcelona. ICMAB-CSIC

The surface properties of Cu(111), Ag(111) and Au(111) are evaluated using strictly localized basis sets. These surfaces present metallic and extended properties that are *a-priori* difficult to deal within a local-basis approach. We explore methodologies to enhance the basis sets of the surface atoms in order to accurately describe surface properties such as surface energies, surface states and work functions. In this way, the advantages of local basis computations (namely: efficiency, optimum size scaling and a natural description of bonding in real space) can be retained without loss of accuracy in the metallic surface description.

Main Topic: A6 Surfaces

Electronic structure of metal atoms at ceria and zirconia surfaces

Ricardo Grau-Crespo[1], *Norge C. Hernandez*[2], *Javier F. Sanz*[2], *Nora H. de Leeuw*[1]

1. Department of Chemistry, University College London, UK
2. Departamento de Fisica-Quimica, Universidad de Sevilla, Spain.

Catalysts consisting of noble metals supported on ceria or zirconia are known to be active in many reactions of technological interest, including low-temperature CO oxidation and the water-gas shift reaction. We have used DFT calculations to investigate the interaction of metal atoms and small particles with the support surfaces. We have shown that Pd deposited on ceria can reduce surface Ce cations, in agreement with recent experimental evidence. A similar but even more complex behaviour is predicted for atomic gold, which can adopt positive, neutral or negative charge states, depending on the adsorption site. On the other hand, the adsorption of gold at non-defective zirconia surfaces does not lead to any charge transfer behaviour, but we found that the substitution of gold in lattice positions at a zirconia surface induces a dramatic change in the redox properties of the surface, which becomes easily reducible thanks to Au(III) - Au(I) transitions.

Main Topic: A6 Surfaces

DFT Studies of TiO_2 (110) and Cu Surfaces

Piotr Kowalski[1], *Bernd Meyer*[2], *Dominik Marx*[1]

1. Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany
2. Friedrich-Alexander-Universität Erlangen-Nürnberg, D-91052 Erlangen, Germany

Using DFT-based ab-initio calculations in combination with a thermodynamic formalism we investigate the properties of TiO_2 (110) surface. We have calculated the relative stability of various structural models of the nonpolar, mixed-terminated TiO_2 (110) surface in contact with a surrounding gas phase at finite temperature and pressure. Adsorption and desorption of H, H_2O, as well as the formation of O vacancies were considered. Assuming thermodynamic equilibrium between the surface and an oxygen, hydrogen and water containing atmosphere, we constructed a phase diagram of the lowest free energy surface structures. For a wide range of temperatures and pressures we find that water will be adsorbed at the surface. At full monolayer coverage, a molecular adsorption of water is preferential. In the low coverage limit, however, a dissociative adsorption becomes energetically more favorable. The most stable adsorption site for hydrogen atoms is on-top of the bridging O atoms. Surprisingly, we find that in thermodynamic equilibrium the bridging O atoms can not be fully saturated which hydrogen, but only a maximum coverage of about 0.6 monolayer can be reached. The formation energy for O vacancies is found to be rather high so that O defects should only form at extreme oxygen poor conditions.

Cu surfaces are interesting from technological point of view as methanol, a key material for the synthesis of organic materials, is made catalytically from gas containing CO, CO_2 and H_2 in presence of a $Cu/ZnO/Al_2O_3$ catalyst. Especially Cu/ZnO shows a much higher catalytic activity for the methanol formation from synthesis gas than pure Cu. It is believed that the morphological changes of the Cu particles on the ZnO support due to a strong metal-support interaction (wetting/dewetting) is the source of this higher catalytic activity. We use DFT-based ab-initio calculations to identify the reactive sites on the Cu particles which might be responsible for the higher catalytic activity. In particular we investigate the adsorption of hydrogen and dissociated formic acid on clean as well as defective (steps/terraces) Cu surfaces. As the rate determining step in the methanol formation is most likely the hydrogenation of formate to dioxomethylen and formaldehyde, we aim in determination of the role of defects (steps/terraces) in hydrogenation of formate. If we can establish that there exists a linear relationship between the dissociative adsorption of formic acid and the activation barrier for formate hydrogenation, so called "volcano plots" can be derived, which allow to identify optimal values for the adsorption energy and the activation barrier, which then can be related to structural configurations.

Main Topic: A6 Surfaces

Molecular Switches at Surfaces: The Role of Van Der Waals Interactions

Erik McNellis[1], *Joerg Meyer*[1], *Karsten Reuter*[1]

1. Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Molecules that by external stimuli may be reversibly switched between different defined states are envisioned as a key component of a future molecular nanotechnology. For the latter, it is particularly the molecular function when the switch is stabilized at a solid surface that is of key interest.

Using density-functional theory (DFT) with a gradient-corrected (GGA) functional we carry out a detailed characterization of the metastable structures of the prototypical molecular switch azobenzene at close-packed coinage metal surfaces. We obtain a range of switch-surface interactions that goes from weak physisorption at Au(111) to a reversal in the stability of the gas-phase cis and trans molecular conformations at Cu(111).

In view of the known inadequacies of present-day GGA functionals in the description of long-range van der Waals interactions, we check on these findings considering corrections from semi-empirical pair potential schemes. While corrections to the gradient are small enough to leave adsorbate geometries essentially unchanged, the obtained adsorption energy corrections are substantial, in certain cases significantly altering the pure DFT picture. We discuss this, and the discomforting differences obtained between the employed semi-empirical schemes in the greater context of molecular adsorption at metal surfaces.

Main Topic: A6 Surfaces

First principle study of hydrogen bonded molecular networks on Au(111) surface

Manh-Thuong Nguyen, Daniele Passerone, Carlo A. Pignedoli, Matthias Treier
and Roman Fasel

Empa, Swiss Federal Laboratories for Materials Testing and Research,
nanotech@surfaces laboratory, Duebendorf and Thun, Switzerland

The formation of Perylene-3,4,9,10-tetracarboxylic Dianhydride and Diaminoterphenyl molecular networks deposited on Au(111) are studied in our laboratory by means of scanning tunneling microscopy (STM). From the experimental investigations, ordered concurring molecular structures and their electronic structures are obtained, calling for an atomistic theoretical explanation. As the first step in our theoretical work, consisting both of localized basis set based and plane wave pseudo-potential based calculations, we study the molecular systems with planar configurations, mimicking the fact that molecules lie on the surface. Afterwards, we study these systems with the presence of Au(111) surface. Our simulations show that the mixing-phase molecular network is stabilized by hydrogen bonding, explaining exactly the molecular phase regimes explored by STM, and the influence of the surface on the relative binding energy of different molecular networks is determined to be weak.

Main Topic: A6 Surfaces

CO_2 bonding with metallic surfaces: an ab-initio study

Maria Peressi[1,2], *Michele Rizzi*[1,2], *Xun-Lei Ding*[2]

1. Departement of Theoretical Physics, University of Trieste, Strada Costiera 11, I-34014 Trieste,Italy
2. CNR-INFM DEMOCRITOS National Simulation Center, Trieste, Italy

The peculiarity of the interaction of CO2 with Ni(110) with respect to other metallic surfaces has been recently pointed out by combined theoretical and experimental studies [1]. A deeper investigation including the analysis of the electron localization function and simulations of scanning tunneling microscopy images is presented here.

The role of steps, of undercoordinated surface sites and other defects are also exploited. Preliminar results for adsorption on a NiCu alloy are also discussed, in order to gain information about the possibly different behaviour of the Ni and Cu metals with respect to the CO2 interaction.

[1] Ding et al., PHYSICAL REVIEW B 76, 195425 (2007).

P 00126

Main Topic: A6 Surfaces

Energy and stress at semiconductor surface steps, using a combined ab-initio and classical potential approach

Marcello Rosini[1,2], *Peter Kratzer*[1,3], *Rita Magri*[2]

1. Fritz-Haber Institut der Max Plank Gesellshaft, Berlin, Germany
2. Dipartimento di Fisica Università di Modena e Reggio Emilia, Modena, Italy
3. Fachbereich Fisik, Universität Duisburg-Essen, Duisburg, Germany

Semiconductor quantum dots and nanowires are of crucial importance in nanoscience and nanotechnology, owing to their peculiar structural, electronic, and optical properties that can be usefully exploited for novel applications. These systems are generally grown on surfaces by epitaxial techniques such as the Stranski-Krastanov growth mode [1], where nanostructures spontaneously nucleate when the wetting layer (WL) thickness is higher than a critical value [2,3]. It has been experimentally observed that nanostructure nucleation occurs preferably at surface defects such as steps [2,3,4].

To address this point, we study here the stability and strain distribution at semiconductor surface steps. We have considered InAs(001) WLs of thickness 1.75 monolayers (that is, corresponding to the critical coverage at which nucleation takes place) deposited on bulk GaAs. On the WL different types of steps (*A* and *B*) are considered, with different step edges, on a □$_2$(2x4) surface reconstruction. For each step, the surface energy, the step energy, and the surface stress are calculated using first-principles pseudopotentials method. We have found the most stable step geometries and the corresponding strain distributions.

To treat the involved large supercells, we have developed an approach where the topmost layers of the surface are treated fully quantum-mechanically using ab-initio calculations, while the layers below are treated using classical Abell-Tersoff interatomic potentials, optimized for surface calculations [5].

[1] I. N. Stranski, and L.Karstanov , S*itzungsber. Akad. Wiss. Wien, Math Naturwiss. Kl. IIb* **146**, 797 (1938).
[2] F. Arciprete, E. Placidi, V. Sessi, et al., *Appl. Phy s. Lett.* **89**, 041904 (2006)
[3] E. Placidi, F. Arciprete, M. Fanf oni, et al., *J. Phy s.: Cond. Matt.* **19**, 225006 (2007)
[4] S. I. Molina, M. Varela, et al., *Appl. Phys. Lett.* **91**, 143112 □(2007)□
[5] T. Hammerschmidt, P. Kratzer, and M. Scheffler, *Phys. Rev. B* **77**, 235303 (2008), and subsequent errata.

The relaxation of vibrational excitation of adsorbates on semiconductor surfaces

Sung Sakong and *Peter Kratzer*

Fachbereich Physik, Universität Duisburg-Essen, Lotharstr. 1, 47048 Duisburg

On semiconductor surfaces, the laser-induced vibrational excitation of adsorbates is relaxed into lattice vibrations of the substrate through both, coupling between vibrations and the vibration-phonon interaction. The electron-hole pair excitation is energetically forbidden, since the vibrational energy is much smaller than the band gap. In this case, the vibrational lifetime is relatively long (order of ns) and the vibrational energy is predominantly dissipated into several small-energy vibrational quanta and phonons. Within the weak phonon-vibration interaction regime, the system can be described by a system-bath Hamiltonian, and the relaxation process is determined by first-order time-dependent perturbation theory. In this framework, we demonstrate how the rate of energy dissipation of the CO stretching on the Si(100) and the H-Ge stretching on Ge(100) surfaces can be calculated from first principles. The vibrational excitations of the adsorbate are accurately described by the multi-dimensional potential energy surface which must be evaluated with DFT accuracy, because of the importance of anharmonic coupling between vibrational modes. However, lattice vibrations around room temperature are considered to be mostly harmonic. Thus it is sufficient to evaluate the phonon properties of the underlying semiconductor substrates with the force field method. This has the advantage that sufficiently many phonon modes can be calculated easily. Finally, the lifetime of vibrational modes and energy dissipation channels are evaluated through Fermi's golden rule. The theoretical results are compared to the experiments using the pump-probe sum frequency generation method. Furthermore, we will demonstrate the control of the lifetime for the H-Ge stretching on Ge(100) using isotope co-adsorption.

Main Topic: A6 Surfaces

Magnetic surface of diluted magnetic oxides: Co- ZnO.

N. Sanchez, S. Gallego and M.C. Muñoz

Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid 28049, Spain

First principles calculations of the O surfaces of Co-ZnO show that substitutional Co ions develop large magnetic moments which long-range coupling depends on their mutual distance. The local spin polarization induced at the O atoms is three times larger at the surface than in the bulk, and the surface stability is considerably reinforced by Co. Moreover, a robust ferromagnetic state is predicted at the Oxygen (0001) surface even in the absence of magnetic atoms. The occurrence of surface magnetic moments correlates with the number of p-holes in the valence band of the oxide, and the distribution of the magnetic charge is, even in the absence of spin-orbit interaction, highly anisotropic.

Main Topic: A7 Spectroscopies

STM spectroscopy of supramolecular metallocomplexes

P.Müller[1], *M. S. Alam*[2], *R.W. Saalfrank*[3], *J. Kortus*[4], *A. Postnikov*[5], *L. K. Thompson*[6], *J.-M. Lehn*[7]

[1]Department of Physics, Universität Erlangen-Nürnberg, Germany
[2]Department of Physics, University of Dhaka, Bangladesh
[3]Institut für Organische Chemie, Universität Erlangen-Nürnberg, Germany
[4]Institut für Theoretische Physik. TU Bergakademie Freiberg, Germany
[5]Laboratoire de Physique des Milieux Denses, Université Paul Verlaine, Metz, France
[6]Department of Chemistry, Memorial University, St. John's, Newfoundland, Canada
[7]ISIS, Université Louis Pasteur, Strasbourg, France

As the contrast in STM images mixes both topographic and electronic effects in a complicated way, mapping of complex molecules is not straightforward. However, scanning tunneling spectroscopy (STS) measurements reveal direct information about the energy levels close to molecules Fermi level. Using our home built STM working under ambient conditions, we succeeded to combine high resolution topography mapping with simultaneous current-voltage characteristics measurements on single molecules deposited on HOPG surfaces. We have investigated a series of supramolecular metallo-complexes involving coordinated metal ions. By comparing with DFT calculations, we confirmed that the weakest bonds, i.e. the supramolecular coordination interactions, dominate the molecular orbitals near the Fermi level of the molecule. Our method allows a selective mapping of the functional units within the supramolecular architecture, even if these units are embedded into a complex set of organic ligands. We observed this behaviour in all of our investigated molecules.

Main Topic: A7 Spectroscopies

Validation of the projector augmented-wave methods for the calculation of solid-state NMR properties of transition metal compounds.

J. Cuny[1, 2], *L. Le Pollès*[1,2], *R. Gautier*[1,2],
C. J. Pickard[3], *J.-B. d'Espinose de Lacaillerie*[4]

[1] Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France
[2] Université européenne de Bretagne
[3] School of Physics & Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom
[4] Laboratoire de Physico-Chimie des Polymères et des Milieux Dispersés, UMR-CNRS 7615, ESPCI, 75231 Paris Cedex 05, France

Since the 1980s, the expansion of solid-state NMR has increased significantly owing to the development of new techniques that enable high resolution to be achieved even in the solid state. For inorganic compounds without protons or fluorine atoms, the chemical shift and the quadrupolar interactions are the two dominant interactions responsible for the appearance of the NMR spectra. The corresponding parameters give information about the atomic structure of the compound under investigation. It appears that in many cases, the complexity of the experimental results requires a theoretical analysis for their complete understanding. Until recently, only quadrupolar interaction parameters could be calculated using periodic DFT calculations. Pickard and Mauri presented a formalism, named GIPAW, for the *ab initio* calculation of all-electron NMR chemical shifts in insulators using pseudopotentials [1]. We present the application of two pseudopotential based methods, projector augmented-wave (PAW) and gauge-including projector augmented-wave (GIPAW), for the calculation of quadrupolar coupling and chemical shift tensors of ^{95}Mo. Validation of those methods is performed on a series of ternary molybdates. The different approximations employed as well as the influence of the crystallographic structures used for the calculations are intensively examined. Computed quadrupolar interaction parameters are compared with the one obtained using an all-electron method [2]. Those parameters as well as chemical shift parameters are also compared with experimental data [3].

[1] C. J. Pickard, F. Mauri *Phys. Rev. B* **2001**, *63*, 245101.
[2] K. Schwarz, P. Blaha, G. K. H. Madsen *Comp. Phys. Commun.* **2002**, *1-2*, 71.
[3] J. Cuny, S. Messaoudi, V. Alonzo, E. Furet, J.-F. Halet, E. Le Fur, S. E. Ashbrook, C. J. Pickard, R. Gautier, L. Le Pollès *J. Comput. Chem.* **2008**, *29*, 2279.

Main Topic: A7 Spectroscopies

Multiple Scattering Approach to Valence Band and Resonant Photoemission

F. Da Pieve[1] *and P.Kruger*[2]

1. ETSF, PCPM, Université Louvain La Neuve, Belgium
2. ICB, Department de Nanoscience, Université de Bourgogne, Dijon, France

Valence band photoemission and resonant photoemission are widely used spectroscopic techniques. In particular, energy and angle resolved ultraviolet photoemission is a powerful technique for mapping energy bands of solids, while resonant photoemission has often been exploited to study the local electronic structure and the retainment or not of atomic features. The LMTO method has been used for the calculation of self consistent potentials in the atomic sphere approximation while the final calculation of the cross section is done in a real space multiple scattering framework. For valence band photoemission we show that a dual behaviour between itinerant and well localized electronic states is observed when analyzing the anisotropy of diffraction patterns, respectively in the cases the analysis is performed in energy resolved or energy integrated mode. Resonant photoemission has been studied with applications to Fe and TiO2 and several preliminary encouraging results on the constant initial state spectra (showing the typical Fano profile) are presented.

Main Topic: A7 Spectroscopies

First-Principles Investigation of Electronic, Structural and Vibrational Properties of a-Si_3N_4

Luigi Giacomazzi[1], *Paolo Umari*[2]

1. CNR-INFM/Democritos National Simulation Center and the Abdus Salam International Centre for Theoretical Physics (ICTP), Strada Costiera 11, I-34014, Trieste, Italy.
2. CNR-INFM/Democritos National Simulation Center, Theory @ Elettra Group, Area Science Park Basovizza, I-34012 Trieste, Italy

Using a density-functional scheme, we present a study of electronic, structural and vibrational properties of amorphous silicon nitride (a-Si_3N_4). Through the use of Car-Parrinello molecular dynamics methods, we generate a structural model which shows a network formed mainly by regular SiN_4 tetrahedra and featuring a small fraction of over- and under-coordinated atoms. The electronic structure of this model is investigated by calculating the quasiparticle density of states through a many-body GW approach. The investigated structural properties include the angular distributions, the atomic arrangements in the first-neighbor shells, and the pair correlation functions. In reciprocal space, we have calculated the neutron total structure factor for which the comparison with available experimental data gives overall good agreement. We then obtain the vibrational frequencies and eigenmodes and we analyze the vibrational density of states through its decomposition into N and Si weights. Using a methodology based on the application of finite electric fields, we derive dynamical Born charge tensors and Raman coupling tensors. We address the dielectric properties, in particular we calculate the real and imaginary parts of the dielectric function, including the high-frequency and static dielectric constants. Furthermore from the knowledge of the dielectric function we calculate the infrared absorption spectrum that is found to accord with experimental data. Finally we carry out Raman spectra calculations that show a fair agreement with available experimental spectra of amorphous silicon nitride.

Main Topic: A7 Spectroscopies

Electron-phonon contribution to the photoemission kink of $La_{2-x}Sr_xCuO_4$

Feliciano Giustino[1], Marvin L. Cohen[2], Steven G. Louie[2]

1. Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom
2. Department of Physics, University of California at Berkeley, California 94720, USA, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

During the past decade a number of high-resolution angle-resolved photoemission experiments have been performed in order to probe the low-energy quasiparticle dynamics of high-temperature copper oxide superconductors. Of direct relevance to the theory of cuprate superconductivity is the anomaly observed at the binding energies of 50-80 meV along the nodal quasiparticle dispersions of several families of cuprates, including in particular $La_{2-x}Sr_xCuO_4$ (LSCO) [1]. This anomaly – referred to as the low-energy photoemission kink – is generally interpreted as the renormalization of the quasiparticle velocity resulting from an electron-boson interaction. However, no consensus has been reached yet on the nature of the boson mode involved, the main contenders being spin fluctuations and optical phonons. If the bosonic renormalization and the associated kink proved to be of phononic origin, then the associated electron-phonon coupling would be large enough to play an important role in the mechanism of high-temperature superconductivity. Here we present first-principles calculations of the role of the electron-phonon interaction in the photoemission spectra of optimally doped and overdoped LSCO. Our calculations indicate that the phonon-induced renormalization of the electron energies and the Fermi velocity is almost one order of magnitude smaller than the effect observed in photoemission experiments. Therefore, our analysis rules out the electron-phonon interaction as the exclusive origin of the observed kink in LSCO [2]. Similar conclusions have been reached in a recent study of the related compound $YBa_2Cu_3O_7$ [3].

[1] A. Lanzara *et al.*, Nature **412**, 510 (2001).
[2] F. Giustino, M. L. Cohen, S. G. Louie, Nature **452**, 975 (2008).
[3] R. Heid, K.-P. Bohnen, R. Zeyher, D. Manske, Phys. Rev. Lett. **100**, 137001 (2008).

Main Topic: A7 Spectroscopies

Vibrational study of 1-methylpyridinium aldoxime chloride based on Raman and FT-IR spectra and b3lyp/6-31++G(d,p) calculation of 1-methylpyridinium aldoxime cation normal modes

Vlasta Mohaček-Grošev[1], *Blaženka Foretić*[2], *S. Kovač*[3]

1. Ruđer Bošković Institute, Bijenička cesta 54, 10002 Zagreb, Croatia
2. Faculty of Medicine, University of Zagreb, Šalata 3, 10000 Zagreb, Croatia
3. J.J. Strossmayer University of Osijek, F. Kuhača 20, 31000 Osijek, Croatia

We have recorded FT-IR and Raman spectra of the 1-methylpyridinium-4-aldoxime chloride and iodide in different conformations of aldoxime group, E and Z. All calculations were performed using the Gaussian 03 suite of programs [1]. In calculation, the geometry of 1-methylpyridinium-4-aldoxime cation was optimized using B3LYP,6-31++G(d,p) method. The aim of the study is to assign selected bands and attempt to correlate the structural features of the title compound with observed spectral changes.

Pyridinium aldoximes are known as antidotes given to patients in the cases of acute poisoning by organophosphorus compounds such as pesticides and chemical warfare nerve agents, which cause long-term inactivation of acetylcholinesterase. The enzyme can be reactivated by nucleophiles that accept a serine-bound phosphate, such as cation of pyridinium aldoxime. The agents comprising quaternary nitrogen that promotes binding in the catalytic site were an early triumph of rational pharmacology based on deductions from classic structure-reactivity relations [2].

References

1. Gaussian 03, Revision E.01, M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada , M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J.Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Orokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q.Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz , I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople. Gaussian, Inc., Wallingford CT, **2004**.
2. I. B. Wilson and S. Ginsberg, Biochim. Biophys. Acta **18** (1955), 168–170.

Main Topic: A7 Spectroscopies

lluminating Graphene Nanostructures

Deborah Prezzi[1,2], *D. Varsano*[1,2], *A. Ruini*[1,2], *A. Marini*[3], *and E. Molinari*[1,2]

1. S3-INFM-CNR Natl. Research Center, Modena, Italy
2. Dipartimento di Fisica, Università di Modena e Reggio Emilia, Modena, Italy
3. Dipartimento di Fisica, Università di Roma 'Tor Vergata', Roma, Italy

Recent advances in the synthesis of single layered graphite have focused the attention on novel carbon-based systems, graphene nanoribbons (GNRs) [1,2,3]. The possibility of patterning graphene sheets in a controllable manner opens exciting opportunities also in view of novel phenomena occurring under light excitation as well as nanoscale optoelectronics applications. We discuss the main characteristics of optical excitations in armchair nanoribbons by means of ab-initio many-body calculations. Our theoretical approach includes both self-energy corrections and excitonic effects through the GW-BSE formalism, providing full understanding of excited-state properties. Electron-hole interaction is found to suppress the van Hove singularities -as known for other 1D systems- and introduces strongly bound excitonic peaks. We analyse different geometries and show that strong exciton binding is accompanied by relevant effects of the ribbon termination [4]. Based on simple prototype structures, we discuss the effect of the width modulation on confinement and optical response [5] and new strategies to control local excitations in graphene nanostructures.

[1] Z. Chen, Y.-M. Lin, M. J. Rooks and P. Avouris, Physica E 40, 228 (2007).
[2] M. Y. Han, B. Ozyilmaz, Y. Zhang, and P. Kim, Phys. Rev. Lett. 98, 206805 (2007).
[3] see e.g. X. Li et al, Science 319, 1229 (2008).
[4] D. Prezzi, D. Varsano, A. Ruini, A. Marini, and E. Molinari, Phys. Rev. B 77, 041404 (2008).
[5] D. Prezzi et al., submitted (2008).

Main Topic: A10 Materials Design

Electronic Properties of Graphene with Adsorbed Atoms

Marcos Veríssimo-Alves[1], *Jean-Christophe Charlier*[1]

1. Unité de Physico-Chimie et de Physique des Matériaux (PCPM), European Theoretical Spectroscopy Facility (ETSF), Université catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium

Since its recent synthesis [1], graphene has attracted a great deal of attention as an interesting prototype to investigate 2D physics and nanoelectronics. Two possibilities for confining electrons in 1D using graphitic-like structures are carbon nanotubes, in which electron mobility is restricted to the tube's axial direction, and carbon nanoribbons, in which confinement arises both from intrinsic 2D structure and finite width.

Recently Chernozatonskii *et al* have proposed, through DFT calculations [2], that lines of H atoms adsorbed on top of graphene sheets could confine carriers to a narrow strip centered on these lines. These lines of H induce a band gap whose value depends on the spacing between them. The adsorption of species other than H could entail different chemical dopings, providing yet another way of tailoring the conductivity of graphene.

The goal of the present study is to investigate the effect of lines and strips of different adsorbed chemical species, namely H, K and F, as donors or acceptors on graphene, in the DFT-LSDA framework. For H (a donor), we explore topologies of adsorption different from those proposed in Ref. [2], which are energetically more stable and allow for a net spin moment. For F (an acceptor), we find that the topology of the adsorbed atoms can make graphene semiconducting or metallic, the latter having localized electronic states at the Fermi energy. Strips of K (a donor) in an arrangement similar to the 2x2 coverage observed experimentally over the surface of graphite, induce rather delocalized states over the sheet, rendering it metallic. Our results suggest that a high degree of control over the deposition techniques will be needed if one is to use this kind of system as a building block for nanoelectronics.

[1] K. S. Novoselov, *et al*, Science **306**, 666(2004).

[2] L. A. Chernozatonskii, *et al*, Appl. Phys.Lett. **91**, 183103 (2007).

Main Topic: A7 Spectroscopies

NMR J-coupling in the solid state by first-principles calculations

Jonathan R. Yates[1], *Sian A. Joyce*[2], *Anne-Christine Uldry*[3] *Chris J. Pickard*[3]

1. Materials Department, University of Oxford, UK 2. Tyndall National Institute, Ireland 3. School of Physics and Astronomy, University of St. Andrews, UK

NMR J-coupling is an indirect interaction of the nuclear magnetic moments mediated by bonding electrons, and provides a direct measure of bond strength and a map of the connectivities of a system. In solution-state NMR, J-coupling measurements can often be obtained from one dimensional spectra where the multiplet splitting in the peaks is clearly resolved. However, in the solid-state, this is often not the case as these splittings are typically obscured by the broadenings from anisotropic interactions. In recent years, bond correlation experiments, in particular, those employing spin-echo magic angle spinning techniques, have resulted in accurate measurements of J-coupling in both inorganic and organic systems.

To complement and support these advances in experimental technique we have recently developed a first principles method to calculate J-coupling in solid-state systems[1]. Like the GIPAW approach to computing NMR chemical shifts (www.gipaw.net), our method is formulated within density functional theory and the planewave-pseudopotential framework.

We present applications of the method to compute Si-O-P and P-O-P couplings in inorganic materials, and to the prediction of hydrogen bond mediated N-N couplings in molecular crystals. In the latter case we demonstrate the influence of the crystal lattice on the observed solid-state J-couplings[2].

1. Sian A. Joyce, Jonathan R. Yates, Chris J. Pickard, and Francesco Mauri J. Chem. Phys. 127, 204107 (2007)
2. Sian A. Joyce, Jonathan R. Yates, Chris J. Pickard, Steven P. Brown J. Am. Chem. Soc., 130, 12663 (2008)

Main Topic: A8 Catalysis and Electrochemistry

ATOMIC PATHWAYS TOWARD THE SYNTHESIS OF FULLERENES AND TRIAZAFULLERENES FROM POLYCYCLIC AROMATIC HYDROCARBONS

Giulio Biddau[1], *Pablo Pou*[1], *Gonzalo Otero*[2], *Jose Angel Martin-Gago*[2] *and Ruben Perez*[1]
[1]*Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, E-28049 Madrid, Spain;* [2]*Instituto de Ciencia de Materiales de Madrid – CSIC, E-28049 Madrid, Spain*

True fullerene-based molecular electronics is actually limited by the current production methods. Standard methods, such as graphite vaporization, do not permit a real control on size, and, particularly, on doping (e.g. heterofullerenes and endohedral fullerene). This has promoted an intense research activity directed towards more rational and efficient synthesis methods.
We have recently achieved the formation of closed fullerenes (C_{60}) and triazafullerenes ($C_{57}N_3$) by thermal annealing using polycyclic Aromatic Hydrocarbons (PAHs) adsorbed on Pt(111) surfaces[1]. The PAHs ($C_{60}H_{30}$ and $C_{57}N_3H_{33}$) chosen as precursors for fullerenes and triazafullerenes (C_{60} and $C_{57}N_3$), are characterized by easy synthesis and doping processes, paving the way to the formation of doped fullerene with specific characteristics.

In this communication, we focus on the theoretical aspects of that work and present large scale first principles DFT calculations using both an efficient local orbital basis [2-3] and standard plane-wave approaches [4-5]. These simulations give support for the interpretation of the experiments that confirm the feasibility of the formation process and provide insight into the atomic pathways leading from the planar PAHs to the closed fullerenes and triazafullerenes. In particular, we characterize the adsorption and STM images of both the planar precursors and the final closed molecules, considering different overages and the influence of surface defects (like surface vacancies). Furthermore, we explore the closure process for partially- and fully-dehydrogenated precursors with the NEB method [6], identifying the relevant steps and showing that the energy barriers are low enough so they can be overcome with the available thermal energy during the annealing process.

Figures

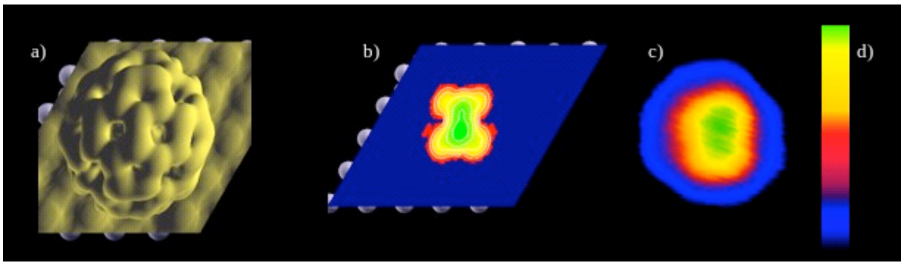


Fig.1: Adsorption of C_{60} on a dimer configuration on a Pt(111)-(5x5) unit cell. Both the charge density isosurface (a) and the charge density contours on a plane at 0.19 nm above the top carbon atoms (b) show a characteristic two-fold symmetry, with an elongated feature and a significant contribution coming from the pentagons, in agreement with the experiments (c). (d) The colour scale ranges from 0 to 0.4 nm.

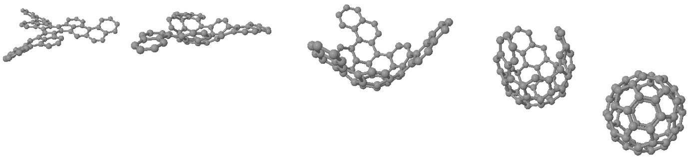


Fig.2: Closure process for the fully-dehydrogenated PAHs towards the C_{60} fullerene.

References:
[1] Otero G, Biddau G *et al*, Nature **464**, 865-869
[2] Jelinek P. *et al,* Phys. Rev. B., **71** 235101.
[3] Lewis J.P. *et al*, Phys. Rev. B, **64**, 195103
[4] Segall M.D *et al*, Cond. Matt. **14**(11), 2717-2743
[5] Kresse G, Phys. Rev. B **47**,C558
[6] Henkelamn G, J. Chem. Phys. **113**, 9901-9904

Main Topic: A8 Catalysis and Electrochemistry

First principles study of Nitrogen and Ammonia with electrified Palladium surfaces.

Lorenzo Paulatto[1], *Stefano de Gironcoli*[1]

1. Scuola Internazionale Superiore di Studi Avanzati (SISSA), I-34014 Trieste, Italy and CNR-INFM DEMOCRITOS National Simulation Center, I-34014 Trieste, Italy

The industrial process for Ammonia synthesis involves Fe-based catalysts at high pressure (≈ 100 bar) and temperature ($450 - 500$ °C). Recently, ambient pressure Ammonia production, in the $570 - 750$ °C temperature range, has been reported at the Palladium cathode of a proton conducting cell-reactor [1-2]. The mechanism of this electrocatalytic Ammonia formation has not yet been clarified but it has been suggested that, in the experimental conditions, Nitrogen hydrogenation may precede molecular dissociation. Within this work we present a first-principle study of the interaction of Nitrogen, Hydrogen and Ammonia with flat and stepped Palladium surfaces, in presence of an external electric field. Our study is based on the Projector-Augmented Wave (PAW) formulation of Density Functional Theory (DFT) in the Quantum-ESPRESSO distribution.

[1] George Marnellos and Michael Stoukides, Science 282, 98 (1998);

[2] George Marnellos, Stergios Zisekas, and Michael Stoukides, Journal of Catalysis 193, 8087 (2000).

Main Topic: A8 Catalysis and Electrochemistry

Molecular Dynamics Simulations of Binding of Metal Catalyst Nanoparticles to Carbon Nanostructures by using ReaxFF

C.F. Sanz-Navarro[1], *P.O. Åstrand*[2], *A.C.T. van Duin*[3], *W.A. Goddard III*[3] *and P. Ordejón*[1]

1. Centro de Investigación en Nanociencia y Nanotecnología - CIN2 (CSIC-ICN), Campus de la UAB, E-08193 Bellaterra, Spain.
2. Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim 7491, Norway.
3. Materials and Process Simulation Center, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA.

Carbon nanofibers have attractive properties as support materials for catalyst nanoparticles. Nonetheless, there is still a need for more insights into the actual atomic structure of a metal particle interacting with carbon nanostructures. Detailed information on the local structure of adhered nanoclusters is still inaccessible to direct experimental imaging. In contrast, molecular dynamics (MD) simulations can provide atomistic structural information of a nanoscale system. In addition, the Reax force field (ReaxFF) aims to achieve a good compromise between accuracy and computational efficiency. We present novel results of MD simulations of platinum and nickel clusters adsorbed on several different carbon supports by using the ReaxFF. This work seeks to give insights into recent experiments that have found a high correlation between carbon nanofiber-induced strain and catalytic activity of Ni clusters. We show how some metal atoms are detached from the surface of the nanoclusters over time scales unreachable by electronic-structure methods. The adatom migration is compensated by a rearrangement of the atomic structure of the cluster. We also show differences in the bond length distribution of the cluster when adsorbed to carbon nanocones with different radii as well as differences found between Pt and Ni clusters. Finally, we brief preliminary results on diffusion of oxygen, hydrogen and carbon atoms over the adsorbed metal cluster.

Main Topic: A8 Catalysis and Electrochemistry

Palladium in selective hydrogenation catalysis

N. Seriani[1], *F. Mittendorfer*[1], *G. Kresse*[1]

1. Fakultät für Physik and Center for Computational Materials Science, Universität Wien, Sensengasse 8/12, A-1090 Vienna, Austria

Hydrocarbonaceous species deposited on a palladium catalyst heavily influence activity and selectivity of the catalyst for reactions of partial hydrogenation of hydrocarbons. The exact nature of these phases and their role are still unclear. We have employed density functional theory together with molecular dynamics and genetic algorithms to investigate the Pd-C-H configuration space and the thermodynamic stability of possible phases. A complex interplay of carbon and hydrogen is found. The results are corroborated by the comparison of calculated core level shifts for the various Pd-C-H phases with XPS spectra of palladium catalysts under operation conditions. These results shed light on the complex Pd-C-H interactions and give insight into the mechanisms of partial hydrogenation catalysis.

Main Topic: A8 Catalysis and Electrochemistry

Free energies of redox (electron transfer) reactions of iodides in solution

Yoshitaka Tateyama[1,2]

1. International Centre for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
2. PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Chemical reactions with electron transfer (ET) in solution, so called 'redox reactions', play crucial roles in diverse topics such as electrochemical cell and catalysis. Adopting the 'energy gap' (ionization potential) formulation of Marcus theory and the thermodynamics integration/perturbation schemes, we have demonstrated ab initio free energy calculation methods for redox reactions with bond breaking/formation coupled to ET [1-3].

I applied these methods to redox reactions associated with iodide and triiodide ions in solution. These iodides are often used as a redox couple in several applications, and also related to famous iodine titration. However the atomistic mechanisms of the redox reactions haven't been fully understood.

My calculations of redox free energies and reaction pathways of several elementary processes of this redox couple indicate that reduction and bond breaking are competitive in the solvated triiodide systems and there seems a significant solvent dependence. In the presentation, I will show the detailed free energy diagrams and the reaction pathways and discuss the potential of this redox couple from the application points of view.

[1] Y. Tateyama, et al., J. Chem. Phys. **122**, 234505 (2005).
[2] J. Blumberger et al., J. Chem. Phys. **124**, 064507 (2006).
[3] Y. Tateyama et al., J. Chem. Phys. **126**, 204506 (2007).

Main Topic: A9 Chemical Reactions and Kinetics

Hot adatom motion tackled from first principles

Jörg Meyer[1], *Karsten Reuter*[1]

1. Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Germany

The initial stages of the oxidation of metal surfaces are still far from being understood – despite their essential importance for example in the field of oxidation catalysis. In view of the exothermicity of the dissociative adsorption of oxygen molecules at most metal surfaces, one fundamental hitherto largely unaddressed question concerns the energy dissipation into the substrate. If this is sufficiently slow, it could give rise to a transient mobility of the adsorbed, but not yet equilibrated oxygen atoms. This so called 'hot adatom motion' has already been suggested as a possible explanation for experimental data [1-2].

In order to address this issue by first-principles theory we separate the molecular encounter with the surface into two stages: At large distances from the surface, substrate mobility can still be neglected and we focus our density-functional theory calculations on the six-dimensional potential-energy surface (PES) representing the molecular degrees of freedom. Performing extensive molecular dynamics (MD) runs on this suitably interpolated PES we evaluate the steering of thermal molecules into specific entrance channels. The corresponding molecular orientations and positions at intermediate heights above the surface form then statistically relevant starting geometries for first-principles MD trajectories of the remaining dissociation path that consider a full substrate mobility in large surface unit-cells.

Aiming to extract kinetic parameters that will provide the basis for a reliable description of the dissociation process in coarse-grained statistical simulations, we carefully analyze the detailed insight into the heat dissipation inside the still finite simulation cell, using the O_2 dissociation on Pd(100) as a showcase.

1. H. Brune, J. Wintterlin, R. J. Behm and G. Ertl *Phys. Rev. Lett.* **68**(5), 1992, 624.
2. J. Wintterlin, R. Schuster and G. Ertl *Phys. Rev. Lett.* **77**(1), 1996, 123.

Main Topic: A10

Origin of the unusually large band-gap bowing and the breakdown of the band-edge distribution rule in the Sn_xGe_{1-x} alloys

Wan-Jian Yin and Xin-Gao Gong
Department of Physics and Surface Science Laboratory, Fudan University, Shanghai 200433, China
Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

The unusual nonlinear behaviors of the band gaps in Sn_xGe_{1-x} alloys are investigated using first-principles calculations. We show that the large bowing of the direct band gap is induced by the disordering effect. Moreover, we calculated individual contribution of the band-edge states and found that the bowing of the conduction band edge is much larger than the bowing of the valence band edge, although the natural valence band offset between Ge and Sn is larger than the natural conduction-band offset. The breakdown of the band-edge distribution rule is explained by the large lattice mismatch between Ge and Sn and the large deformation potential of the band-edge states.

Main Topic: A10 Materials Design

Finding New Graphitic Structures – The Search for Generalised Haeckelites using a Genetic Algorithm

M.I.J. Probert[1]

1. Department of Physics, University of York, Heslington, York, YO10 5DD, U.K.

There has been much interest recently in graphene, as it has many novel electronic properties. It is well known that carbon can adopt many different structural forms, and there is a generalised class of graphitic structures known collectively as Haeckelites[1] that have been theoretically proposed. In this work, we present the results of an *ab initio* based search for new Haeckelite structures. By using a recently developed Genetic Algorithm[2] that has been specifically targeted at periodic systems, we find a number of new structures that were not previously known. As well as the structures, we also present some predictions for the basic electronic properties of these new materials.

[1] H. Terrones et al., Phys. Rev. Lett. **84**, 1716 (2000)

[2] N. L. Abraham and M. I. J. Probert , Phys. Rev. B **77**, 134117 (2008); N. L. Abraham and M. I. Probert Phys. Rev. B **73**, 224104 (2006)

Main Topic: A10 Materials Design

Electronic and structural properties of germanium dioxide

Shoichiro Saito[1]*, Kikuji Hirose*[1] *and Tomoya Ono*[1]

1. Department of Precision Science and Technology, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Although the first transistors were all germanium-based, currently silicon is by far the most widely used semiconductor for electronics, for example because it can withstand much higher temperatures. For the past several decades, improved transistor performance has been mainly accomplished by scaling the transistor dimensions resulting in a higher circuit speed, higher packing densities, and less power consumption. At present, the aggressive scaling of the SiO_2 gate dielectric leads to unacceptably high gate leakage currents. As an alternative to the scaling approach, enhancing the channel carrier mobility can increase the drive current, which has recently led to a renewed interest in germanium because of its intrinsically higher carrier mobility. Unlike structure of silicon dioxide, however, structure of germanium dioxide is not well-known. In the case of atomic structure of silicon dioxide, there are four distinct O-Si-O angles near the tetrahedral angle of 109.5 degree. Because these angles are "stiff"[1] and do not change easily, interface structures of SiO_2/Si are carefully determined.

In this study, to obtain the knowledge for construction of interface atomic structures of GeO_2/Ge, the atomic structure of the germanium dioxide bulk is examined by a first-principles calculation. We studied four crystalline phases of the germanium dioxide, quartz, cristobalite, tridymite, and rutile. The most stable phase is the rutile structure of germanium dioxide. This result is consistent with the former calculation[2]. We also found that the O-Ge-O bonding angles change by 4 degree, while the O-Si-O bonding angles change by 2 degree in the case of the cristobalite structure. In the case of the other crystalline phases, the variations of the bonding angles of germanium dioxide bulk are larger than those of silicon dioxide bulk. Thus, we can conclude that the O-Ge-O bonding angles are soft compared to the O-Si-O bonding angles. In the presentation, we give the details of this simulation.

[1]J.R.Chelikowsky, H.E.King, Jr. and J.Glinnemann, Phys. Rev. B. **41**, 10866 (1990).

[2]D.M. Christie and J.R. Chelikowsky, Phys. Rev. B **62**, 14 703 (2000).

Main Topic: A10

Possible Polymorphism in perylene PR179

T. Zykova-Timan[1]*, P.Raiteri*[2]*, M.Parrinello*[3]

1. Computational Science, Department of Chemistry and Applied Biosciences,
ETH Zurich, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Present address: Institut fuer Physik, Johannes-Gutenberg-Unive
rsitaet Mainz,
Staudinger Weg 7, 55099 Mainz

2. Computational Science, Department of Chemistry and Applied Biosciences,
ETH Zurich, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Present address: Nanochemistry Research Institute, Curtin Univer
sity of Technology, GPO Box U1987, 6845, Perth, Western Australia.

3. Computational Science, Department of Chemistry and Applied Biosciences,
ETH Zurich, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

The polymorphism of an industrial important pigment (PR179) was studied with a combination of standard crystal structure prediction and metadynamics. The former provided a starting set of candidate polymorphs whose structural and thermal stability were then probed by metadynamics. Moreover, metadynamics allowed for exploring the free energy surface to look for other possible polymorphs that were not included in the original set. Our calculations indicate that two structures have a high structural stability and are therefore good candidates to be found in experiments. The lower energy phase of the two indeed corresponds to the known polymorph and we suggest that the other might be a metastable polymorph not yet experimentally discovered.

Main Topic: A11 Other applications

Solid-Liquid phase boundaries by a free energy perturbation approach

Stefano Angioletti-Uberti[1], *Mark Asta*[2], *Mike Finnis*[3], *Peter D. Lee*[4]

1. Department of Materials, Imperial College London, Prince Consort Road 20, SW72BP London, UK
2. Department of Chemical Engineering and Materials Science, University of California at Davis, One Shields Ave., Davis, CA, USA

We describe a method for deriving free-energy differences based on a free-energy perturbation (FEP) formalism in an alloy system described by two different potentials. The intended application is the calculation of solid-liquid phase equilibria in alloys using electronic density-functional theory (DFT) accuracy. In order to do so, free energies are calculated with a classical interatomic potential and FEP calculations are used to compute corrections to these reference values. For practical applications of this approach, due to the high computational cost of DFT calculations, it is critical that the FEP calculations converge rapidly with the number of samples used to estimate the characteristic ensemble average. We investigate this issue employing two classical interatomic potential models for Ni-Cu. These two models predict the solid-liquid phase boundary relatively shifted of about 100 K, comparable to the expected difference between a DFT Hamiltonian and a well-fit classical potential. We show that for both pure elements and equiatomic alloys, FEP calculations converge in about a few dozen and a few hundred calculations respectively, to within 1 meV/atom. The results suggest that the proposed methodology could provide a computationally tractable framework for calculating solid-liquid phase equilibria in concentrated alloys with DFT accuracy.

Main Topic: A11 Other applications

Entropy from structural correlation functions

O N Bedoya-Martínez[1,2], *E R Hernández*[2]

1. DMN/SRMP, Centre de Recherches de Saclay, 91191 Gif sur Yvette Cedex, Commissariat l'Energie Atomique, France
2. Institut de Cincia de Materials de Barcelona (ICMAB - CSIC), Campus de Bellaterra, 08193 Barcelona, Spain

The entropy of a given system can be obtained from evaluating the temperature derivative of the Gibbs free energy (or Helmholtz free energy). This is the more accurate way of evaluating entropies; nevertheless, the free energy must be calculated. An alternative approach is to use an expansion of the entropy into n-particle correlation functions [1]. The advantage of this expression of the entropy is that, at least, the correlations of pairs and triples of particles can be obtained from experiments or from MD simulations. In this work we have studied, for realistic systems (liquid metals including Ag, Rh, Cu, Ir, Au, Pt, Pd, Ni, Al, liquid Si and amorphous Si), the convergence of such expansion considering correlation functions up to order 3, and comparing with entropies obtained directly from free energy calculations. We have found that in the case of metals pair correlation functions are sufficient for estimating entropies, while in the case of silicon systems higher order correlation functions are necessary. Such difference is due to the range of correlation in these systems. The metals considered in this study are systems with non directional bonding, while silicon systems do have highly directional bonding. One needs then at least three-particle correlation functions in order to describe correctly the entropy of silicon systems. Nonetheless, we have shown that three-particle correlation functions are not easy to calculate. The structure of the system, then, will be useful for estimating the entropy, if such structure can be described from pair correlation functions.

References

[1] Harold J. Raveché, *J. Chem. Phys*, 55, pp. 2242-2250, 1971.

Main Topic: A11 Other applications

Vibrational properties of the filled tetrahedral compounds LiMgAs and LiCdAs

A. Mellouki[1] , B. Bennecer[1], L. Kalarasse[1], F. Kalarasse[1]

1. Physics Laboratory at Guelma, Faculty of Science and Engineering, University of Guelma, P.O. Box 401, Guelma 24000, Algeria

Abstract: We have studied the dynamical properties of the filled tetrahedral compounds LiMgAs and LiCdAs and the binary analogs AlAs and InAs by employing the plane-wave pseudopotential method within density functional theory. The calculated lattice constants for these compounds are consistent with other local density approximation calculations and they reproduce the trend encountered in the experimental data. The phonon dispersion curves and density of states are calculated by using density functional perturbation theory. The high frequency optic modes in LiCdAs are assigned to Li–As pairs. The force constants of Mg–As and Cd–As are about 43% and 59% higher than those of Li–As, in LiMgAs and LiCdAs respectively, showing the relatively high covalency of the former bonds.

Keys words: Semiconductors, Ab initio calculations, Vibrational properties

Main Topic: **A11 Other applications**

Ab initio coexistence simulations of Lithium melting

D. Alfè[1], *A. Bergara*[2], *E. R. Hernández*[3] *and A. Rodriguez-Prieto*[4]

1. Department of Earth Sciences, University College London, UK
2. Física de la Materia Condensada, Universidad del Pais Vasco, Bilbao, Spain
3. Institut de Cincia de Materials de Barcelona (ICMAB-CSIC), Barcelona, Spain
4. London Centre for Nanotechnology (LCN), University College London, UK.

We report large scale first principles molecular dynamics simulations, aiming at determining the melting behaviour of the low-pressure bcc and fcc phases of Li. We have performed constant pressure simulations [1, 2] in which both solid and liquid phases are put in contact, and the temperature is allowed to adjust until the coexisting value at the imposed pressure results. Calculations have been performed with the Vienna Ab Initio Simulation Package [3] using the Projector Augmented Wave approach [4, 5], with the 1s electrons in the frozen core and the Perdew-Burke-Ernzerhof exchange-correlation functional [6]. Our simulations employ 2000 atoms, and the results obtained thus far are in excellent agreement with the available experimental data [7, 8].

References

[1] I. Souza and J. L. Martins, Phys. Rev. B **55**, 8733 (1997).

[2] E. Hernández, J. Chem. Phys. **115**, 10282 (2001).

[3] G. Kresse and J. Furthmüller, Phys. Rev. B, **54**, 11169 (1996).

[4] P. E. Blöchl, Phys. Rev. B, **50**, 17953 (1994).

[5] G. Kresse and D. Joubert, Phys. Rev. B, **59**, 1758 (1999).

[6] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., **77** (1996).

[7] H. D. Luedemann and G. C. Kennedy, J. Geophys. Res. **73**, 2795 (1968).

[8] R. Boehler, Phys. Rev. B **27**, 6754 (1983).

Main Topic: A11 Other applications

A molecular dynamics study of the phase diagram of carbon employing a neural network potential

Rustam Z. Khaliullin[1], *Thomas D. Kühne*[1], *Hagai Eshet*[1], *Jörg Behler*[2],
Michele Parrinello[1]

1. Department of Chemistry and Applied Biosciences, ETH Zurich, USI Campus, via G. Buffi 13, 6900 Lugano, Switzerland.
2. Lehrstuhl fur Theoretische Chemie, Ruhr-Universitat Bochum, D-44780 Bochum, Germany.

Carbon allotropes possess a wide range of physical properties and are of fundamental and practical importance. In spite of this, the phase diagram of carbon is not well studied experimentally because of the difficulty of accessing the extreme pressures and temperatures required for phase transitions. Computer simulations have had only limited success in modeling the diagram mainly because of the inadequacy of empirical potentials to describe the wide range of interactions in carbon phases and the computational expense of ab initio simulations. We propose to determine the phase diagram involving liquid carbon, graphite, diamond, and high-pressure metallic phases using a recently developed neural-network representation of ab initio potential energy surfaces. This novel methodology provides energies and forces of the ab initio quality with the speed of the empirical potentials. It will be used in combination with thermodynamic integration and metadynamics to address a number of hotly debated questions such as the presence of the reentrant points on the melting curves of graphite and diamond, the possibility of liquid-liquid phase transitions, and the nature of carbon phases at extremely high pressures.

Main Topic: A11 Other applications

First principles study of optical properties of defects in pure and doped amorphous silica

N. Richard[1], L. Martin-Samos[2], S.Girard[1], Y. Ouerdane[3], A. Boukenter[3], J.-P. Meunier[3], V. Cuny[3]

1.CEA-DAM-DIF, Bruyères-le-Châtel, France
2.INFM S^3, Dip. Fisica, Univ. Modena e Reggio E., Modena, Italy
3.Laboratoire Hubert Curien UMR CNRS 5516 , Saint-Etienne, France

Generation mechanisms of radiation-induced point defects in amorphous silica (*a*-SiO2) have been widely studied due to its central role in most of photonics technologies used in harsh environments. Point defects or color centers are generated at the microscopic scale through ionizing or/and “knock-on” processes. At the macroscopic scale, these defects are responsible for the degradation of optical properties of bulk or fiber waveguides. In this study, we focus on Oxygen Deficient Centers (ODC) and theirs effects in optical fibers. Several experimental techniques allow the determination of the nature and properties of point defects. Electron Paramagnetic Resonance (EPR) is used to determine the structural properties and concentrations of paramagnetic centers. Optical Absorption (OA) measurements point out the bands responsible for the radiation-induced attenuation increase of optical fibers. Luminescence measurements can also be used to identify the emitting point defects. To relate a defect structure to its optical bands, a correlation must be found between ESR, OA and luminescence results as a function of dose, temperature or other treatments. This correlation is still difficult to realize. Moreover, the knowledge of the exact composition of the silica in a fiber is often missing.

The most recent *ab initio* method can then bring new insights on the structures, the electronic and optical properties of a particular defect in silica. In this study, in the framework of the Density Functionnal Theory (DFT), in 108 atoms pure and Ge-doped (2.8 mol %) silica-based supercells, we performed a statistical study on the structure and energetic properties of ODC’s. All the 72 oxygen sites in the amorphous silica (a-SiO_2) cell were considered as possible candidates for vacancy formation leading to the study of 72 different Si-ODC (Si-Si) and 144 Ge-ODC (Ge-Si). The distributions of structural parameters and formation energies of the oxygen vacancies are then obtained. The calculated parameters showed a large distribution that can be mainly associated to the different local environments surrounding these defects. Starting from some of these vacancy structures, we used the code SaX to go beyond the DFT and to incorporate many body corrections within the GW approximation and the Bethe-Salpether theory. These methods allow us to calculate electronic properties and the OA bands of oxygen vacancies in silica.

Main Topic: A11 Other applications

Lattice dynamics and specific heat of α - GeTe: a theoretical and experimental study

R. Shaltaf[1], *X. Gonze*[1], *M. Cardona*[2], *R. K. Kremer*[2], *G. Siegle*[2]

1. European Theoretical Spectroscopic Facility, Unit PCPM, Université Catholique de Louvain,B-1348 Louvain-la-Neuve, Belgium
2. Max-Planck-Institut für Festkörperforschung,Heisenbergstr. 1, D-70569 Stuttgart, Germany

We have investigated the dynamical and specific heat of GeTe in its low temperature rhombohedral phase using first-principles density functional theory. We report the phonon dispersion curves, the density of phonon states and temperature dependent specific heat. In contrast to results for other IV-VI materials, we found that the inclusion of spin orbit coupling has a small effect on the calculated phonon frequencies and consequently on the heat capacity. On the other hand, we found that ignoring non-stoichiometric effects of GeTe, leads to discrepancies between the calculated and the measured C_p/T^3. These can be resolved by taking into account the existence of free hole carriers which lead to an increase of C_p/T^3 in agreement with experimental findings. Such increase was found to be due to phonon frequency softening and the corresponding down shift of the density of phonon states.

Main Topic: A11 Other applications (Materials under pressure)

New high-pressure phases of calcium and their finite-temperature phase boundaries

A. M. Teweldeberhan and S. A. Bonev

Department of Physics, Dalhousie University, Halifax, NS B3H 3J5, Canada

The phase diagram of Ca has been studied using first-principles density functional theory. The simple cubic structure hitherto believed to exist between 32 and 109 GPa is found to be mechanically and thermodynamically unstable. Instead we propose two new solid phases with orthorhombic *Cmcm* and *Pnma* structures and determine their finite-temperature phase boundaries. The *Cmcm* structure is base-centered orthorhombic with two atoms per unit cell, while the *Pnma* is simple orthorhombic with four atoms per unit cell. The mechanism driving the computed phase transitions has been investigated.

PROGRAMME

ALL TALKS WILL BE HELD AT THE LEONARDO DA VINCI BUILDING, MAIN LECTURE HALL
POSTER SESSIONS WILL BE HELD AT THE ADRIATICO GUEST HOUSE, LOWER LEVEL 1

	THURSDAY, 8 JANUARY 2009	
8:00	*Registration and administrative formalities* (L. da Vinci Building, Lobby)	
8:50	Welcoming Remarks (L. da Vinci Building, Main Lecture Hall)	Organizers
	SESSION 1: Many-body Techniques for Real Materials	
9:00	Bridging the size gap between density-functional and many-body perturbation theory	Geoffrey Stenuit - CNR-INFM Democritos, Trieste, Italy
9:35	Efficient evaluation of dielectric matrices for *ab-initio* calculations of excited state properties and correlation energies	Giulia Galli - UC Davis, USA
10:10	Band offsets from many-body perturbation theory	Gian-Marco Rignanese - Univ. Catholique de Louvain, Belgium
10:45	*Coffee Break + Registration*	
11:30	Efficient and accurate calculation of exact exchange and RPA correlation energies in ACFD theory	Huy-Viet Nguyen - Hanoi National University of Education, Viet Nam, and SISSA, Trieste, Italy
12:05	Correlation in electronic excitations	Lucia Reining - Ecole Polytechnique, Palaiseau, France
12:40	*Lunch break*	
	SESSION 2: Simulations of Structural Properties	
14:40	Quantum protons in hydrogen bonded systems	Roberto Car - Princeton U., Princeton, USA
15:15	*Ab-initio* random structure searching: A window on structure space	Chris Pickard - St. Andrews, UK
15:50	*Coffee Break + Registration*	
16:35	Quantum Monte Carlo simulations of behavior at extreme conditions	Ron Cohen - Carnegie Institution, USA
17:10	TBC: *Modeling materials at high pressure for earth sciences*	Borje Johansson - Uppsala, Sweden
	POSTER SESSION 1 (venue: Adriatico Guest House, Lower Level 1)	
17:45	Poster setup at Adriatico Guest House	
18:30	Poster session / free discussions - *informal buffet for all participants during the poster session*	
	FRIDAY, 9 JANUARY 2009	
	SESSION 3: 2008 ICTP Prize Ceremony	
8:50	Welcoming remarks and Presentation of the Award	K.R. Sreenivasan - ICTP Director
9:35	LDA+Gutzwiller method for correlated electron systems	Zhong Fang - Center for Quantum Simulation Sciences, CAS, Beijing, China
10:10	Green-Kubo formula for heat conduction in open systems	Abhishek Dhar - Raman Research Inst., Bangalore, India
10:45	*Coffee Break*	
	SESSION 4: Thermal and Electronic Transport	
11:30	Thermal transport at the nanoscale	Davide Donadio - UC Davis, USA
12:05	First-principles studies of single-molecule junction conductance: Links, length, and switching	Jeff Neaton - Molecular Foundry, LBNL, Berkeley, USA
12:40	*Lunch*	
	SESSION 5: Quantum Chemistry	
14:40	Fermion Quantum Monte Carlo in slater determinant spaces: A game of life, death and annihilation	Ali Alavi - Cambridge, UK
15:15	Explicitly correlated ab initio methods for metals	Beate Paulus - Freie Universität Berlin, Germany
15:50	*Coffee Break*	
16:30	Constrained DFT for electron transfer and reaction barrier heights	Troy Van Voorhis - MIT, Cambridge, USA
17:10	Efficient first-principles van der Waals density functional forces	Jose Soler - Universidad Autónoma de Madrid, Spain
	POSTER SESSION 2 (venue: Adriatico Guest House, Lower Level 1)	
17:45	Poster setup at Adriatico Guest House	
18:30	Poster session / free discussions - *informal buffet for all participants during the poster session*	
	SATURDAY, 10 JANUARY 2009	
	SESSION 6: Carbon Nanostructures	
8:50	Introduction of Keynote Speaker	Organizers
9:00	Exploiting the Electronic, Thermal, and Mechanical Properties of Carbon and BN Nanostructures - *Keynote talk in honor of STEVEN LOUIE's 60th birthday*	Alex Zettl - UC Berkeley, USA
9:50	Electron correlation in graphene: band structure and electron-phonon interaction from GW	Claudio Attaccalite - U. del Pais Vasco, San Sebastian, Spain
10:25	Energy gaps in graphene superstructures	Young-Woo Son - KIAS, Seoul, Korea
11:00	*Coffee Break*	
	SESSION 7: Large-scale and Multi-scale Simulation	
11:45	Towards an error-controlled multi-scale catalysis modeling	Karsten Reuter - FHI-MPG, Berlin, Germany
12:20	Computational investigation of DNA derivatives for nano-electronics	Rosa di Felice - INFM-CNR, Modena, Italy
12:55	*Lunch*	
	SESSION 8: Functional Materials	
14:40	DFT studies of FeAs superconductors	Lilia Boeri - MPI-FKF, Stuttgart, Germany
15:15	Hydrogen superconductivity and other superconductors	Gianni Profeta - Università degli Studi dell'Aquila, Italy
15:50	*Coffee Break*	
16:35	Ab-initio pseudopotential calculations of the orbital magnetization	Davide Ceresoli - MIT, Cambridge, USA
17:10	First-principles electrochemistry	Ismaila Dabo - INRIA and Université Paris-Est, France
17:45	Concluding Remarks	