The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

13th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

11 – 13 January 2007
Trieste – Italy

Co-sponsored by:
SISSA – International School for Advanced Studies
INFM DEMOCRITOS National Simulation Center
ESF/Psi-k Network

Organizing Committee:

N. Marzari	MIT, Cambridge, U.S.A.
P. Ordejon	ICMAB-CSIC, Barcelona, Spain
S. Scandolo	the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy

PROGRAMME
ABSTRACTS of INVITED TALKS
and
ABSTRACTS OF POSTERS

http://agenda.ictp.trieste.it/smr.php?1824

PREFACE

This Workshop follows the series started in Oxford, U.K. (1983) and continued in Braunschweig, Germany (1984) and in Trieste, Italy (1987, 1989, 1991, 1993, 1995, 1997, 1999, 2001, 2003 and 2005). Following the tradition of the previous meetings, the Workshop is devoted to recent advances in computational condensed matter physics and materials science, based on realistic calculations of the electronic structure of complex systems.

The activity is being held at the Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy from 11 to 13 January 2007 with the co-sponsorship of the International School for Advanced Studies (SISSA), INFM DEMOCRITOS National Simulation Center and European Science Foundation (ESF-Psi-k) network.

As in previous events of this series, the Workshop consists of invited talks with ample space devoted to discussion.

Theory and Methods:
Density-Functional Theory beyond LDA
    Nanoscience
Time Dependent DFT
Many-Body Techniques for Real Materials
Quantum Monte Carlo
Ab-initio Molecular Dynamics
Large Scale and Multiscale Simulations
Activated Processes
Electronic Transport
Response to External Fields
Simulations in Realistic Environments

Applications:
Biochemistry and Biomaterials
Magnetism and Spintronics
Geophysics
Functional Materials
Surfaces
Spectroscopies
Catalysis and Electrochemistry
Chemical Reactions and Kinetics
Materials Design

Organizing Committee:

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SCIENTIFIC COMMITTEE:

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G. Galli (University of California at Davis, USA)

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Complete List of Participants is available via the following web-page:
http://agenda.ictp.trieste.it/smr.php?1824

PROGRAMME

(as of 18 December 2006)

The Abdus Salam
International Centre for Theoretical Physics

United Nations
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13th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

11 - 13 January 2007

(Miramare, Trieste, Italy)

co-sponsored by:
SISSA – International School for Advanced Studies
INFM DEMOCRITOS National Simulation Center
ESF/Psi-k Network

PRELIMINARY PROGRAMME

(updated as of 20 December 2006)

ALL LECTURES WILL BE HELD AT THE
ICTP MAIN BUILDING - MAIN LECTURE HALL

Organizers / Local Organizers:
N. Marzari, P. Ordejon and S. Scandolo

THURSDAY, 11 JANUARY 2007

08.30 - 09.15 **REGISTRATION / ADMINISTRATIVE FORMALITIES**
Reception area of the Main Building
(subsequently: during every coffee break in reception)

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09.15 – 09.30 OPENING – Introductory Remarks

09.30 – 10.30 Keynote talk in honor of **Alfonso BALDERESCHI's 60th Birthday**

Federico CAPASSO (Harvard University, Cambridge, USA)
Harnessing quantum fluctuations: design, physics and
Nanomechanics of Casimir-Lifshitz forces and QED torques

10.30 – 11.00 *Coffee Break + Registration*

SESSION 1: Electrons and Phonons

11.00 – 11.30	**Francesco MAURI** (Univ. Pierre et Marie Curie, Paris, France) Non-adiabatic vibrations in doped graphene
11.30 – 12.00	**Aitor BERGARA** (Univ. del Pais Vasco, Bilbao, Spain Pressure Induced Complexity in Light Alkalies
12.00 – 12.30	**Nicolas LORENTE** (Univ. Paul Sabatier, Toulouse, France) Vibronic effects in electron transport through atomic and molecular systems
12.30 – 12.50	**Feliciano GIUSTINO** (Univ. of California @ Berkeley, USA) Electron-Phonon interaction with electron and lattice Wannier Functions and superconductivity in Boron-doped diamond
12.50 – 14.30	*Lunch Break*

SESSION 2: Dispersion Forces in Density-functional Theory

14.30 – 15.00	**Bengt LUNDQVIST** (Chalmers Univ. of Tech., Gothenburg, Sweden) Promising path to DFT for sparse matter – a functional with Van der Waals interactions
15.00 – 15.30	**Pablo GARCIA-GONZALEZ** (UNED, Madrid, Spain) Many-body and time-dependent DFT methods to evaluate electron total energies
15.30 – 15.50	**Stefano de GIRONCOLI** (SISSA & DEMOCRITOS National Simulation Center) van der Waals coefficients in DFT: a simple approximation for the polarizability
15.50 – 16.20	*Coffee Break + Registration*

SESSION 3: Excitations: GW and Bethe-Salpeter

16.20 – 16.50	**Fabien BRUNEVAL** (Ecole Polytechnique, Palaiseau, France) Self-consistent GW electronic structure of solids
16.50 – 17.20	**Patrick RINKE** (Fritz-Haber-Institut, Berlin, Germany) Exact-exchange based quasiparticle energy calculations applied to (transition) metal nitrides: ScN and InN

17.20 – 17.40	**Paolo UMARI** (SISSA & DEMOCRITOS National Simulation Center) Fast GW calculations using ultra-localized Wannier functions
18.30 – 20.00	***POSTER SESSION 1*** *Poster Gallery (behind Main Lecture Hall)* *as well as Lecture Room C (terrace level)*

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FRIDAY, 12 JANUARY 2007

09.00 – 10.00	Keynote talk in honor of **Raffaele RESTA's 60th Birthday** **Joshua ZAK** (Technion, Haifa, Israel) Von Neumann Lattices and Wannier Functions

SESSION 4: Polarization and Magnetization

10.00 – 10.30	**Timo THONHAUSER** (Rutgers University, Piscataway and MIT, Cambridge, USA) Orbital magnetization in periodic solids and its connection to NMR
10.30 – 11.00	**Umesh WAGHMARE** (JNCASR, Bangalore, India) Geometric phases, distribution of electron charge centers, Wannier functions and bonding in materials
11.00 – 11.30	*Coffee Break + Registration*

SESSION 5: Time-Dependent Density-functional Theory

11.30 – 12.00	**Kieron BURKE** (University of California, Irvine, USA) Time-dependent density functional theory: An overview
12.00 – 12.30	**Stefano BARONI** (SISSA & DEMOCRITOS National Simulation Center Turbocharging TDDFT using Lanczos chains
12.30 – 13.00	**Ilya TOKATLY** (Moscow Instit. Of Electronic Tech., Russia / Univ. Erlangen-Numberg, Germany) Quantum mechanics in a co-moving frame: An emergence of time-dependent deformation functional theory
13.00 – 14.30	*Lunch Break*

SESSION 6: Spintronics

14.30 – 15.00	**Stefan BLUEGEL** (KFA, Julich, Germany) Title to be confirmed
15.00 – 15.30	**Hadi AKBARZADEH** (Isfahan Univ. of Tech., Iran) Ab-initio study of Co_2MnSi (001) surface and $Co_2MnSi/GaAs$ (001) interface
15.30 – 16.00	*Coffee Break + Registration*

SESSION 7: Surfaces, Interfaces and Clusters

16.00 – 16.30	**Annabella SELLONI** (Princeton University, USA) Defects on TiO_2 surfaces
16.30 – 17.00	**Massimiliano STENGEL** (Univ. California @ Santa Barbara, USA) First-principles calculations of capacitors at finite bias potential
17.00 – 17.30	**Xin-gao GONG** (Fudan University, Shanghai, China) Pressure Induced the Phase Transition in Nano-cluster and Nano-tubes

SESSION 8: From Inorganic to Bio

17.30 – 18.00	**Dario ESTRIN** (University of Buenos Aires, Argentina) Exploring Chemical Reactivity in Biological Systems with hybrid QM/MM Methods
18.00 – 18.20	**Moumita SAHARAY (JNCASR, Bangalore, India)** Car-Parrinello molecular dynamics simulation studies on supercritical carbon dioxide
19.30 – 21.30	***POSTER SESSION 2*** *– (with wine, ham and cheese)* *Poster Gallery (behind Main Lecture Hall)* *as well as Lecture Room C (terrace level)*

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SATURDAY, 13 JANUARY 2006

09.00 – 10.00	Keynote talk in honor of **Roberto CAR's 60th Birthday** **Marvin COHEN** (University of California, Berkeley, USA) The Evolution of the Pseudopotential Method for Computational Materials Science

SESSION 9: Complexity in Phase Space

10.00 – 10.30	**Gerbrand CEDER** (MIT, Cambridge, USA) The first principle prediction of crystal structure by combining Knowledge methods with first principles energy methods
10.30 – 11.00	**Thomas KUEHNE** (ETH Zurich, Lugano, Switzerland) An efficient and accurate Car-Parrinello-like approach to Born-Oppenheimer molecular dynamics
11.00 – 11.30	**Alessandro De VITA** (Universita' di Trieste, Italy) Mechanical properties of brittle solids studied with the "learn on the fly" hybrid MD scheme
11.30 – 12.00	*Coffee Break + Registration*

SESSION 10: Quantum Monte Carlo

12.00 – 12.30	**David CEPERLEY** (Univ. of Illinois @ Urbana-Champaign, USA) Quantum Monte Carlo Simulations of Dense Hydrogen
12.30 – 13.00	**Richard NEEDS** (Cambridge University, UK) Equation of state and Raman frequency of diamond from quantum Monte Carlo
13.00 – 14.30	*Lunch Break*

SESSION 11: Functional Materials

14.30 – 15.00	**Igor ABRIKOSOV** (Linkoping University, Sweden) Ab-initio theory of alloys: new possibilities for materials design
15.00 – 15.30	**David DRABOLD** (Ohio University, Athens, USA) Simulations of Hydrogenated Amorphous Silicon

SESSION 12: Strong Correlations: SIC, LDA+U and DMFT

15.30 – 16.00	**Antoine GEORGES** (Ecole Polytechnique, Palaiseau, France) Electronic structure of strongly correlated systems with Dynamical mean-field theory: status report and perspectives
16.00 – 16.30	**Igor MAZIN** (Naval Research Laboratory, Washington, USA) Charge ordering as alternative to Jahn-Teller distortion
16.30 – 17.00	*Coffee Break + Registration*
17.00 – 17.30	**Eva PAVARINI** (IFF, Juelich, Germany) Electronic structure trends in transition metal oxides: The NMTO+DMFT approach
17.30 – 18.00	**Axel SVANE** (University of Aarhus, Denmark) Self-interaction correlation calculations of f-electron materials
18.00 – 18.15	CONCLUDING REMARKS

ABSTRACTS

OF

INVITED TALKS

(in alphabetical order of Speaker
as of 18 December 2006)

Ab initio theory of alloys: new possibilities for materials design.

I. A. Abrikosov

[1]*Department of Physics and Measurements Technology,*
Linköping University, Linköping, Sweden

We will review recent developments in the field of *ab initio* electronic structure theory and its application for studies of complex alloy systems. Basic ideas behind state-of-the-art techniques for first-principles theoretical simulations of the phase stabilities and properties of intermetallic compounds and alloys based on the density functional theory will be outlined. We will concentrate on methods that allow for an efficient treatment of disorder effects [1,2], and illustrate their predictive power with examples.

Three major factors that determine the structure of a material are the valence electron concentration, the difference in electronegativity and the difference in size between its constituents. The ability of the first-principles theory to describe the phase transitions in complex materials upon the change of the electron concentration, and to understand their origin, will be illustrated by the study of anomalous stability of ferritic low Cr steels against the radiation damage [3]. Moreover, we will show that the electronic structure variation with alloy concentration plays the decisive role in the mixing and decomposition thermodynamic of hard coating nanocomposite thin films based on transition metal nitrides [4]. The ability of the *ab initio* materials design will be illustrated by the theoretical optimization of ionic conductivity in doped ceria [5].

[1] I. A. Abrikosov, A. M. N. Niklasson, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. Lett. **76**, 4203 (1996).
[2] L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett. **87**, 156401 (2001).
[3] P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B **73**, 104416 (2006).
[4] B. Alling, A. V. Ruban, A. Karimi, O. E. Peil, L. Hultman, and I. A. Abrikosov, Phys. Rev. B (to be published).
[5] D. A. Andersson, S. I. Simak, N. V. Skorodumova, I. A. Abrikosov, and B. Johansson, "Optimization of ionic conductivity in doped ceria", PNAS **103**, 3518 (2006).

Ab initio study of
Co2MnSi (001) surface and Co2MnSi/GaAs (001) interface

Hadi Akbarzadeh, Nahid Ghaderi, and Javad Hashemifar
Department of Physics, Isfahan University of Technology, Isfahan, Iran

We have studied the electronic and magnetic properties of Co2MnSi (001) surface as well as Co2MnSi/GaAs (001) interface within the frame work of density functional theory. Analyzing the surface band structure of two ideal (CoCo/MnSi and MnSi/CoCo) and several modified surfaces, we found out that the pure Mn termination (MnMn/CoCo) is the only surface that preserves the half metallicity of the system. For other terminations the surface states destroy the half metallicity.

In order to select the appropriate interface of Co2MnSi/GaAs (001), we calculated the phase diagram by ab initio atomistic thermodynamics. Considering the results obtained from phase diagram and suggestions based on the existing theoretical and experimental data, we focused our attention on the ideal MnSi/As and modified MnMn-As terminations. The ideal termination (and consequently also the modified one) has four different possible patterns that can be obtained by considering the continuation along [001] direction of one of the two GaAs fcc sub lattice (either As or Ga) with either Mn or Si. These patterns are labeled as Mn(Ga), Si(Ga), Mn(As), and Si(As). By comparison of the formation energy we further limited our study to Mn (Ga) and Mn (As) as the most favorable patterns. In the case of ideal MnSi-As termination we found out that the spin polarization at the Mn (As) interface is 100% while for Mn (Ga) this value diminishes to 67%. For modified MnMn-As termination the spin polarization for MnMn (Ga) is 100% while for MnMn (As) we found a value of 80%. By investigating the strength of Co-Mn bond in different terminations along with the effect of potential raise up on As we were able to analysis our results. Furthermore, the band alignments were extracted for the majority and minority spin channels.

Pressure Induced Complexity in Light Alkalies

A. Bergara[1,2,3]

[1]*Condensed Matter Physics Department, Faculty of Science and Technology, University of the Basque Country, E-48080 Bilbao, Basque Country, Spain*

[2]*Donostia International Physics Center (DIPC), Manuel de Lardizabal Pasealekua, E-20018 Donostia, Basque Country, Spain*

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(e-mail: `a.bergara@ehu.es`)

Recently reported correlated structural complexity[1] and enhanced temperature superconducting transition[2] in lithium under pressure have increased the interest in light alkalies, otherwise considered as simple and well known systems under normal conditions. Strong modification of bonding and electronic properties in lithium under pressure[3] becomes the origin of its strong departure from the classical nearly free electron like model. In this talk we present an analysis of the pressure induced Fermi surface deformation in lithium and its relation to the observed complexity. According to our calculations, the Fermi surface becomes increasingly anisotropic with pressure and at 8 GPa contacts the Brillouin zone boundary inducing a Hume-Rothery mechanism explaining the *bcc-fcc* transition. Around 30 GPa increasing cooper-like necks and an extended nesting are observed in the Fermi surface in the *fcc* phase, enhancing the electronic susceptibility response function and inducing a strong phonon softening[4]. This softening, besides preluding the transition to complex structures and providing a better understanding of the observed superconductivity[5], is expected to induce other yet unexplored anomalies in compressed lithium. Additionally, we will propose the existence of a new low energy undamped interband collective mode[6] arising with the *bcc-fcc* structural transition in lithium under pressure, which is expected to induce an abrupt plasma edge in the experimentally observable reflectivity and also affect electronic correlations at low energies.

[1] J. B. Neaton and N. W. Ashcroft, Nature **400**, 141 (1999); M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature **408**, 174 (2000).

[2] K. Shimizu, H. Ishikawa, D. Takao, T. Yagi, and K. Amaya, Nature **419**, 597 (2002); V. V. Struzhkin, M. I. Eremets, W. Gan, H. K. Mao, and R. J. Hemley, Science **298**, 1213 (2002); S. Deemyad and J. S. Schilling, Phys. Rev. Lett. **91**, 167001 (2003).

[3] A. Bergara, J. B. Neaton, and N. W. Ashcroft, Phys. Rev. B **62**, 8494 (2000); A. Rodriguez-Prieto and A. Bergara, Phys. Rev. B **72**, 125406 (2005).

[4] A. Rodriguez-Prieto and A. Bergara, Proceedings of the Joint 20th AIRAPT-43rd EHPRG 2005 Conference, cond-mat/0505619; A. Rodriguez-Prieto, A. Bergara, V. M. Silkin, and P. M. Echenique, Phys. Rev. B **74**, 172104 (2006); A. Rodriguez-Prieto, A. Bergara, and V. M. Silkin, accepted for publication in J. Phys. Soc. Jpn. (2007), cond-mat/0607683.

[5] J. S. Tse, Y. Ma, and H. M. Tutuncu, J. Phys.: Condens. Matter **17**, S911 (2005); D. Kasinathan, J. Kunes, A. Lazicki, H. Rosner, C. S. Yoo, R. T. Scalettar, and W. E. Pickett, Phys. Rev. Lett. **96**, 047004 (2006); G. Profeta, C. Franchini, N. N. Lathiotakis, A. Floris, A. Sanna, M. A. L. Marques, M. Luders, S. Massidda, E. K. U. Gross, and A. Continenza, Phys. Rev. Lett. **96**, 047007 (2006).

[6] V. M. Silkin, A. Rodriguez-Prieto, A. Bergara, E. V. Chulkov and P. M. Echenique, to be published (2007).

Self-Consistent *GW* Electronic Structure of Solids

Fabien Bruneval

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c/o USI campus, Via G. Buffi 13, CH-6900 Lugano,
Switzerland

It is known that the Kohn-Sham (KS) density functional theory (DFT) has no theoretical reason to provide meaningful band structures. In accordance with this, the KS band gap systematically underestimates the photoemission band gaps of solids.

In order to cure this shortcoming, the Green's function framework, in particular using the Hedin's *GW* approximation [1], has been extensively used. The *GW* approximation has been successful in describing the band structure of a large range of materials and structures. However, this type of calculation relies on a series of approximations that may fail for more complex cases. The main assumption is that the *GW* calculation is performed as a "one-shot" correction on top of an independent electron calculation (e.g. KS). For instance, the simple oxide Cu_2O is poorly described within KS and therefore also within *GW*. As a consequence, it is impossible to describe the interesting optical spectrum of Cu_2O.

We have implemented a self-consistent *GW* method [2] using the "quasiparticle constrained" scheme of Faleev *et al.* [3]. The self-consistent *GW* approach is more satisfactory from the theoretical point of view and yields high quality band structures. The discussion will be illustrated by a series of materials, ranging from metals to insulators. Emphasis will be put on the role of the band structure on the absorption spectrum of Cu_2O [4].

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

[2] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B, **74** 045102 (2006).

[3] S. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004).

[4] F. Bruneval, N. Vast, L. Reining, M. Izquierdo, F. Sirotti, and N. Barrett, Phys. Rev. Lett. in press (2006).

Time-dependent density functional theory: An overview

Kieron Burke Department of Chemistry and Department of Physics
UC Irvine
http://chem.ps.uci.edu/~kieron/dft/

This talk will be an overview of the state-of-the-art of TDDFT. This formalism has been very successful in going beyond ground-state DFT to extract electronic excitations of molecules and clusters, and has become a routine tool in quantum chemistry. Applications to bulk systems have been slower, due to problems with the locality of common density functionals.

I hope to quickly discuss: basic ideas and theorems, linear response theory, applications and performance, complications for solids, new functionals, and new applications, including molecular electronics.

For background, some recent references include:

Time-dependent density functional theory, edited by M. Marques, C.A. Ullrich, F. Noguiera, A. Rubio, K. Burke, and E.K.U. Gross (Springer, Heidelberg, 2006).
(http://www.springer.com/east/home/physics?SGWID=5-10100-22-173664005 detailsPage=ppmmedia)

and

Time-dependent density functional theory: Past, present, and future,
K. Burke, J. Werschnik, and E.K.U. Gross, J. Chem. Phys. 123, 062206 (2005)

Harnessing quantum fluctuations: design, physics, and nanomechanics of Casimir-Lifshitz forces and QED torques

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Division of Engineering and Applied Sciences
Harvard University, Cambridge MA 02138
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The Casimir/Lifshitz force is the attraction between uncharged metallic or dielectric surfaces due to quantum mechanical fluctuations of the electromagnetic field. We will first review our work on MicroElectroMechanicalSystems (MEMS) in which the Casimir force between metallic surfaces at submicron distances has been measured with high precision and exploited for the quantum mechanical actuation of MEMS and for the realization of a new class of nanometric position sensors.[1,2] Next recent experiments on tuning the Casmir force using hydrogen switchable mirrors and thin metallic films will be presented.[3,4] The last part of the talk will describe new experiments aimed at detecting the predicted vacuum torque between suitable birefringent materials as well as repulsive force between solids separated by a liquid, in which the dielectric constant at imaginary frequency of the latter is intermediate between those of adjacent media over a large frequency range.[5,6] The critical role of *repulsive* Casimir/Lifshitz forces in these experiments and their applications in the realization of virtually frictionless bearings and related devices will be discussed. For a brief review of the above work see Ref. 6

This research was partly supported by the National Science Foundation Nanoscale Science and Engineering Center under Contract #: PHY0017795. Support from the Harvard University Center for Nanoscale Systems is also acknowledged.

1. H.B. Chan, V.A. Aksyuk, R. N. Kleiman, D.J. Bishop, F. Capasso, *Phys. Rev. Lett.* **87**, 211801 (2001)
2. H.B. Chan, V.A. Aksyuk, R. N. Kleiman, D.J. Bishop, F. Capasso, *Science*, **291**, 1941 (2001).
3. D. Iannnuzzi, M. Lisanti , F. Capasso, *Proc. Nat. Acad. Sci.* **101**, 4019 (2004)
4. M. Lisanti, D. Iannnuzzi, F. Capasso, *Proc. Nat. Acad. Sci.* **102**, 11989 (2005)
5. J. Munday, D. Iannuzzi, Y. Barash, F. Capasso, *Phys. Rev. A* **71**, 042102 (2005)
6. D. Iannuzzi, M. Lisanti, J. Munday, F. Capasso, *Solid-State Comm.* **135**, 618 (2005)

The first principle prediction of crystal structure by combining knowledge methods with first principles energy methods.

Gerbrand Ceder Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, USA.

The prediction of structure is a key problem in computational materials science that forms the platform on which rational materials design can be performed. For many materials chemistries standard DFT approaches are highly accurate in selecting the true ground state of a system form a small set of candidate structures, though notable exceptions exist. *Finding* ground states by traditional optimization methods on quantum mechanical energy models is difficult due to the complexity and high dimensionality of the coordinate space. An unusual, but efficient solution to this problem can be obtained by merging ideas from heuristic and ab initio methods: In the same way that scientist build empirical rules by observation of experimental trends, we have developed machine learning approaches that extract knowledge from a large set of experimental information and a database of over 15,000 first principles computations, and used these to rapidly direct accurate quantum mechanical techniques to the lowest enery crystal structure of a material. *Knowledge* is captured in a Bayesian probability network that relates the probability to find particular crystal structure at a given composition to structure and energy information at other compositions. We show that this approach is highly efficient in finding the ground states of binary metallic alloys and can be easily generalized to more complex systems

Quantum Monte Carlo Simulations of Dense Hydrogen

David CEPERLEY
University of Illinois Urbana-Champaign
U.S.A.

Abstract

Quantum Monte Carlo (QMC) methods are the most accurate and general methods for computing total electronic energies. However, in general, they have been limited to high temperatures or to zero temperature. In recent years, we and others have been working on methods that utilize the Born Oppenheimer approximation to allow simulations coupling the correlated quantum systems and a system of ions. Using quantum Monte Carlo, one estimates the Born-Oppenheimer energy change for a movement of the ions which is then used in a Monte Carlo simulation of the ionic degrees of freedom. The quantum effects of the ionic degrees of freedom and the boundary conditions on the phase of the wavefunction can be integrated over. We have performed simulations of dense hydrogen down to temperatures of 300K. Our results show features of the phase diagram qualitatively different than computed using DFT, for example in the melting of the atomic solid and in the atomic-molecular transition in the liquid.

The Evolution of the Pseudopotential Method for Computational Materials Science

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Abstract: A general discussion will be given of the background related to the development of pseudopotential theory from Fermi's original work to its use in current computational approaches to study materials. The evolution from calculations for electronic and structural properties of bulk materials, surfaces, and interfaces, to predicting properties like superconductivity will be described. The motivating concepts will be emphasized, and a description of some current activities will be given with a focus on the properties of nanostructures. The influence of Roberto Car's contributions, particularly the Car-Parrinello Method, will be discussed.

van der Waals coefficients in DFT : a simple approximation for the polarizability

Stefano de Gironcoli[1,2], and Huy Viet Nguyen[1,2,3]
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[2] *DEMOCRITOS MOdelling Center for Research In aTOmistic Simulations,*
via Beirut 2-4, I 34014, Trieste (Italy),
[3] *Physics Faculty, Hanoi University of Education,*
136 Xuan Thuy, Cau Giay, Hanoi, Vietnam.

abstract

Long-range dispersion (van der Waals) interactions appear and play a crucial role in many systems. Density Functional Theory (DFT), within the Local Density and the Generalized Gradient Approximations for exchange-correlation energy is known to fail in describing properly van der Waals interactions, while approaches from the exact adiabatic connection formula of this quantity are computationally impracticable, except for few simple systems. We show here that a simple, computationally fast procedure to calculate van der Waals coefficients in DFT framework with reliable results can be developed from a simple approximation for the kinetic energy functional. Results of calculations applied to atomic and molecular systems strongly support the validity of the method in capturing essential part of long range correlations. These results may give useful information for constructing an exchange-correlation functional which includes van der Waals interactions in a natural way.

Mechanical properties of brittle solids studied with the "learn on the fly" hybrid MD scheme.

Alessandro De Vita
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I will describe the main features and some initial applications of a molecular dynamics method which combines quantum mechanical embedding and classical force model optimization into a unified scheme free of the boundary region and transferability problems which these techniques, taken separately, involve.[1] The scheme is based on the idea of augmenting a classical force model by incorporating, at run time, extra quantum mechanical information necessary to ensure accurate trajectories. This is achieved through a parameter-fitting procedure in which a classical force field is adjusted "on the fly" to reproduce accurate results computed using (any number of) quantum mechanical "black box" engines.[2] The approach can be used to achieve both transferability and accuracy starting from a force model of only moderate complexity, and deals in novel ways with some traditionally difficult issues of embedding methods, such as modelling the boundaries between quantum and classical regions and ensuring energy conservation [3-6]. The scheme is useful to investigate "multi-scale" phenomena, requiring large model systems in which strongly coupled sub-regions must be modelled concurrently at different levels of precision. Test examples include point-defect diffusion and the effect of chemical impurities on dislocation diffusion. Fracture behaviour in covalent solid will be looked at in more detail. In particular, the Si(111)[1-10] crack system is found to reconstruct under uniaxial stress, predicting that a local "tip blunting" mechanism driven by elastic energy release at the crack tip region can operate in a brittle material at subcritical loads. Moreover, recent experimental observations on Si single crystals subject to [110]-oriented uniaxial tensile stress show that crack propagation is easily deflected from the (110) plane, so that novel (111) surfaces are created in a characteristic "zig-zag" crack propagation behaviour. MD simulations of model Si(110)[1-10] systems up to 200000 atoms using the SIESTA DFT code as quantum engine reveal that the effect is due to a dynamic instability in the bond breaking process, which is reached only after a crack acceleration phase. The simulations also provide a description of crack propagation as the result of a delicate interplay between dynamical stress concentration, bond-breaking and surface reconstruction phenomena taking place at the advancing crack tip region, which are at the basis of the "lattice trapping" effect in brittle materials.

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Simulations of Hydrogenated Amorphous SIlicon

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Hydrogenated amorphous silicon is an important material for myriad applications. Despite thirty years of intense experimental and theoretical research, important puzzles remain. For applications, the role of H in the network and photoresponse are of special importance. We describe the energetics and dynamics of both atomic and molecular hydrogen in realistic structural models. We then discuss thermally driven H hopping, and will emphasize the importance of the Si dynamics in determining hopping events. Photo-induced degradation of the material is modeled with a simple scheme to handle photo-excited network dynamics. By combining the results of these simulations with proton NMR measurements from Craig Taylor's group, it appears that the light-soaking leads to formation of particular dihydride configurations. These calculations are undertaken using the local orbital density functional code SIESTA.

Exploring Chemical Reactivity in Biological Systems with hybrid QM/MM Methods

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We present a hybrid Quantum Mechanics Molecular Mechanics (QM/MM) implementation developed to deal with large molecular complexes. It is particularly suited to study relatively large systems in which the environment effects are important, as in the case of an enzyme active site immersed in a protein matrix, or a solute in a condensed phase. In the QM/MM scheme, a region of the system receives a quantum-mechanical description, while the environment is treated at the molecular mechanics level using the biomolecules Amber force field. The QM calculations are performed with the SIESTA code, a DFT scheme based on finite basis sets and pseudopotentials, which makes the overall implementation very efficient. We will present results obtained with this scheme for the following problems:
(i) conversion of chorismate to prephenate catalyzed by the enzyme chorismate mutase of *Bacillus Subtilus*. (ii) modulation of oxygen affinity in heme proteins by proximal, distal and dynamical effects. (iii) detoxification of nitric oxide by the truncated hemoglobin N of *Mycobacterium Tuberculosis*.

Many-body and time-dependent DFT methods to evaluate electron total energies

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Since the pioneering works by Lein *et al.* [Phys. Rev. B **61**, 13431 (2000)] and Holm *et al.* [Phys. Rev. B **57**, 2108 (1998); Phys. Rev. Lett. **83**, 788 (1999)] there is an increasing interest in the evaluation of electron total energies using techniques either based on Many-body Perturbation Theory (MBPT) or on Time-dependent Density Functional Theory (TDDFT). These approaches are much more expensive than conventional implementations of the Kohn-Sham (KS) theory. However, they provide a truly first-principles description of electron-electron correlations without resorting to mean-field-like approximations, thus overcoming many well-known limitations of the KS-LDA or KS-GGA. In particular, these methods allow the proper description of van der Waals forces between arbitrary species, regardless their specific electronic nature.

In the first part of this talk, I shall briefly summarize and compare both MBPT and TDDFT methods, focusing on their conceptual and technical advantages and limitations when applied to calculate electron total energies. In the second part, I shall concentrate on a recent application of TDDFT, where structural properties and vibrational spectra of hexagonal Boron Nitride are obtained [Phys. Rev. Lett. **96**, 136404 (2006)]. This system is a paradigmatic example of layered material, where weak (dispersion-like) and strong (covalent) bonds coexist. The Kohn-Sham LDA and, specially, GGA badly fail when evaluating the layer-layer interactions. On the contrary, the in-plane and out-of-plane bonding is well described using TDDFT, also when the layers are pulled apart. This work paves the way for further implementations of truly *ab-initio* applications in systems where standard Kohn-Sham techniques lack of predictive accuracy.

[*] Work made in collaboration with Andrea Marini, Ángel Rubio, Rex Godby, John Dobson, Jeil Jung, Kris Delaney, Patrick Rinke, and Tim Gould

Electron-Phonon Interaction with Electron and Lattice Wannier Functions and Superconductivity in Boron-doped Diamond

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The electron-phonon interaction plays a crucial role in a variety of physical phenomena, ranging from conventional superconductivity to polaronic transport in organic materials. While experimental investigations of the manifestation of electron-phonon interaction in the excitation spectra of electrons and phonons have witnessed impressive advances in recent years, first-principles calculations of the electron-phonon coupling still remain computationally demanding for simple systems, and lie beyond the reach of current capabilities for most complex systems. In this talk I will present a first-principles methodology which we have recently developed for carrying out robust and effective calculations of the electron-phonon interaction with millions of k points in the Brillouin zone. This technique consists in evaluating the electron-phonon vertex in the electronic and lattice Wannier representation, and then using the result to obtain the vertex for arbitrary electron and phonon momenta in the Bloch representation. I will demonstrate this methodology by discussing the phonon self energy and the pairing mechanism in superconducting boron-doped diamond. We modeled boron-doped diamond by considering both a virtual crystal approximation and a large supercell containing boron, and by sampling the Brillouin zone with a million of k points. Our calculations indicate that the localized vibrational modes associated with the boron atoms are crucial to the superconducting pairing insofar they enable scattering processes with large momentum transfer. I will show that a dense Brillouin zone sampling is essential for a correct interpretation of the pairing mechanism in boron-doped diamond. This work was done in collaboration with J. R. Yates, I. Souza, M. L. Cohen, and S. G. Louie at the University of California, Berkeley.

Pressure Induced the Phase Transition in Nano-cluster and Carbon Nano-tubes

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Studies on the phase transition of the nano-cluster and nano-tubes recently become very interesting. In this talk I present a new method for constant-pressure molecular dynamics simulation which is parameter free. This method is especially appropriate for finite systems in which a periodic boundary condition does not apply. I will also show the results on the pressure induced phase transition in carbon nanotubes and nano-clusters, from which one can also easily obtain the equations of states for a finite system under external pressure.

An Efficient and Accurate Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics

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We present a new method to accelerate density functional theory-based ab-initio molecular dynamics simulations. In the spirit of the Car-Parrinello [1] approach, the method circumvents the need to perform fully self-consistent electronic structure calculations. However, in contrast to the original scheme, large integration time steps can be used. To achieve this, we propagate the electronic degrees of freedom in terms of the contra-covariant density matrix in a nearly time-reversible manner by applying the always stable predictor-corrector method [2]. The corrector consists of a single preconditioned minimization step using the idempotency conserving orbital transformation method [3]. In this way sizable minimization steps can be taken, which guarantees that the propagation is performed within a small skin very close to its instantaneous ground state.

Although the applied non-self-consistent energy functional is not variational, the energies thus calculated are a strict upper bound. Deviations from the Born-Oppenheimer surface are small and, more importantly constant, which implies that energy differences are portrayed with great accuracy.

In spite of these excellent properties the incomplete energy minimization and the use of a non-symplectic integrator for the electronic degrees of freedom induces a small dissipative drift. Inspired by ideas of Krajewski and Parrinello [4] we show how this can be rigorously corrected using a properly modified Langevin equation, which leads to correct sampling of the Boltzmann distribution. Furthermore the friction term is so small that the dynamics is also properly reproduced. The method works well irrespective of system type and band gap, so it is very efficient even in simulating large metallic systems.

We implemented these ideas in the mixed Gaussian Plane Wave (GPW) [5] code QUICKSTEP [6] which is part of the publicly available suite of programs CP2K [7]. Using this code we performed extensive tests on liquid semiconductors showing that the accuracy can be maintained throughout. The gain in efficiency ranges from one to two orders of magintude depending on the system.

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Vibronic effects in electron transport through atomic and molecular systems.

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Electron transport on the atomic scale is sometimes classified in two different regimes: tunnelling and ballistic. They correspond to the case of low-conductance because the electron has to tunnel through an isolating barrier, i.e. the vacuum gap in a scanning tunnelling microscope (STM) and the case of high conductance where electrical contact has been established. In the presence of vibrations, transport can be further classified by the strenght of the electron-vibration coupling: from weak interactions where at most the vibrator is excited once, to stronger coupling where the vibrator is multiply excited.

The spectroscopic analysis of vibrations induced on adsorbates on metallic surfaces with an STM [1] belongs to the cases of tunnelling in the presence of weak electron-phonon coupling. I will show that the simulation of inelastic electron tunnelling spectra is needed for determining the excited modes and identifying the measured species. Recently, we have been able to determine the product of an STM-induced reaction on benzene by simulating the spectra of the different possible products [2].

In the tunnelling regime, the strong electron-vibration coupling can be easily attained. In a very specific situation, we show that vibrations can eventually create electronic currents. This is the case of dangling-bond vibrations in a semiconducting surface. Indeed, the otherwise "state-in-the-gap" that is a dangling bond on a Si(111)$\sqrt{3}$x$\sqrt{3}R30°$-B surface, can become connected with the acceptor (boron, B) band via its large electron-vibration coupling. The role of the multiply excited vibration is to permit the electron flow between the tip of an STM and the bulk boron band [3]. I will present experimental and theoretical results on this system.

The high-conductance and weak electron-phonon coupling case corresponds to the ballistic regime. The electron current is not a tunnelling current, and the mean free path of electrons is much larger than the typical dimensions of the atomic objects. Recent experimental data have shown that it is possible to excite localized vibrations in mono atomic gold chains in this regime [4] akin to vibrational spectroscopy in the tunnelling regime. I will briefly review our theoretical work [5] that reveals the modes excited by the ballistic current, as well as the difference between the heating of atomic wires and the dynamics induced on molecules by the STM.

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Promising Path to DFT for Sparse Matter – a Functional with van der Waals Interactions

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The wide world of sparse matter seems now accessible for description by density-functional theory (DFT). To understand biostructures, soft matter, and other abundant sparse systems we must account for both strong local atomic bonds and weak nonlocal van der Waals (vdW) forces between atoms separated by empty space. A fully nonlocal functional, vdW-DF [1] appears in many applications, including layered systems (graphite, boron nitride, and molybdenum sulfide), dimers of benzene, PAH's, doped benzene, and cytosine, polymer crystals, and benzene and naphtalene adsorption on graphite [2], to be promising. This could have great ramifications.

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Non-adiabatic vibrations in doped graphene

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The Born-Oppenheimer approximation (BO) is the standard ansatz to describe the interaction between electrons and nuclei. BO assumes that the lighter electrons adjust adiabatically to the motion of the heavier nuclei, remaining at any time in their instantaneous ground-state. BO is well justified when the energy gap between ground and excited electronic states is larger than the energy scale of the nuclear motion. In metals, the gap is zero and phenomena beyond BO (such as phonon-mediated superconductivity or phonon-induced renormalization of the electronic properties) occur. The use of BO to describe lattice motion in metals is, therefore, questionable. In spite of this, BO has proven effective for the accurate determination of chemical reactions, molecular dynamics and phonon frequencies in a wide range of metallic systems. Graphene, recently discovered in the free state, is a zero band-gap semiconductor, which becomes a metal if the Fermi energy is tuned applying a gate-voltage Vg. Graphene electrons near the Fermi energy have two-dimensional massless dispersions, described by Dirac cones. I will show that a change in Vg induces a stiffening of the Raman G peak (i.e. the zone-center E2g optical phonon), which cannot be described within BO [1,2]. Indeed, the E2g vibrations cause rigid oscillations of the Dirac-cones in the reciprocal space. If the electrons followed adiabatically the Dirac-cone oscillations, no change in the phonon frequency would be observed. Instead, since the electron-momentum relaxation near the Fermi level is much slower than the phonon motion, the electrons do not follow the Dirac-cone displacements. This invalidates BO and results in the observed phonon stiffening. This spectacular failure of BO is quite significant since BO has been the fundamental paradigm to determine crystal vibrations from the early days of quantum mechanics.

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Charge ordering as alternative to Jahn-Teller distortion

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It was pointed out in the seminal paper of Jahn and Teller that a partially occupied degenerate molecular level, often a doubly degenerate E_g level in a cubic ligand field, is unstable against a distortion that splits the level and lowers the total energy of the occupied states. Since then, this effect has been commonly found in solids where it takes a form of a *cooperative* Jahn-Teller (JT) effect (orbital ordering), when the crystal lattice distorts coherently so as to lift orbital degeneracy at each site or, in band language, to split an entire band (*e.g.*, e_g) and thus open a gap at the Fermi level. Upon the gradual delocalization of degenerate electrons, the JT distortion and corresponding orbital ordering becomes less and less favorable, but, as we show, below a crossover region exists with the possibility of lifting degeneracy not by an *orbital ordering*, but by a *charge ordering* (CO): an electron can be transferred from one ion to another, so that, say, the doubly degenerate e_g level on one site will be fully occupied, and on the other site empty. In this paper we demonstrate, experimentally and by first principles calculations, that just such a "JTCO" effect actually occurs in the rare earth nickelates such as $YNiO_3$ and $LuNiO_3$. Apparently this novel phenomenon can also take place in other similar systems.

Equation of state and Raman frequency of diamond from quantum Monte Carlo

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Diamond is an important material with many technological applications, including a key role within high-pressure physics. Diamond anvil cells are used to study the structures of materials and phase transitions under pressure, and to synthesise new materials. Although there have been many experimental studies of the physical properties of diamond, in fact they are not well characterised under very high pressures.

The equations of state (EOS) of many materials can be described over a wide range of pressures by the values of the equilibrium volume V_0, the zero-pressure bulk modulus B_0, and the zero-pressure derivative of the bulk modulus B_0'. The values of V_0 and B_0 for diamond are well established, but there is considerable uncertainty about the value of B_0'. A recent study gave $B_0' = 3.0 \pm 0.1$,[1] although it has been argued that the ruby pressure calibration used should be revised. The most commonly cited value is $B_0' = 4.0 \pm 0.5$,[2] but the large error bar leads to considerable uncertainty in the EOS at high pressures. The Raman frequency of diamond is also of considerable interest, and the possibility of using its volume dependence as a pressure gauge in very-high-pressure diamond-anvil-cell studies has been widely discussed.

We use the variational quantum Monte Carlo (VMC) and the more accurate diffusion quantum Monte Carlo (DMC) methods to calculate the equation of state and Raman frequency of diamond. We make corrections for the effects of zero-point motion and finite temperature effects to enable proper comparison with experiment. DMC gives values of V_0 and B_0 in good agreement with experiment, while for B_0' we obtain 3.8±0.1, which is within error bars of the experimental value reported in Ref. [2], but well outside the error bars of the value reported in Ref. [1]. Our value is close to that obtained within density functional theory using the Perdew-Burke-Ernzerhof (PBE) Generalised Gradient Approximation (GGA).

The Raman frequency of diamond is calculated at several volumes using the frozen phonon method. Our DMC frequency of 1359±4 cm^{-1} calculated at the experimental equilibrium volume is in good agreement with the experimental value of 1333 cm^{-1}. At each volume the VMC and DMC Raman frequencies are a little higher than those obtained from the local density approximation (LDA) and the PBE-GGA.

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Electronic structure trends in transition metal oxides: the NMTO+DMFT approach

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The combination of the first-principles N^{th}-Order Muffin-Tin Orbital (NMTO) method with a modern many-body technique, dynamical mean-field theory (DMFT), in short NMTO+DMFT method, is a powerful approach for elucidating *trends* in the properties of strongly correlated electron systems [1]. In this scheme *material-specific* Hubbard Hamiltonians – and the corresponding basis of Wannier functions – are constructed *ab-initio* by means of the NMTO downfolding technique; the small but realistic Hubbard models obtained with this procedure are then solved with DMFT. After an overview of the approach, as a striking example I will present the Mott metal-insulator transition and orbital-ordering phenomena in a family of $3d$ transition metal oxides [1, 2, 3].

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Exact-exchange based quasiparticle energy calculations applied to (transition) metal nitrides: ScN and InN

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The metal nitride InN and the transition metal nitride ScN have recently received increased attention in the field of opto-electronics. Their electronic band structure – a key quantity for devices – has been difficult to access experimentally (due to growth related problems) and theoretically (due to strong self-interaction effects in the local-density approximation (LDA) to density functional theory (DFT)). Here we show that removing the self-interaction by applying DFT in the exact-exchange optimized effective potential approach (OEPx) correctly predicts ScN and InN to be semiconductors and not (semi)metals as found in the LDA. The OEPx ground state then provides a suitable starting point for quasiparticle energy calculations in the G_0W_0 approximation. Our OEPx+G_0W_0 gap supports recent experimental observations [1] that ScN has a much lower indirect band gap than previously thought [2]. We further show how a meaningful comparison to LDA based G_0W_0 calculations can be constructed that allows us to make contact with self-consistent GW calculations. For InN our OEPx+G_0W_0 band gap of 0.7 eV [3] suggests an intrinsic value at the lower end of the experimentally observed range [4]. Taking the Burnstein-Moss effect into account, the increase of the apparent quasiparticle gap with increasing electron concentration is in good agreement with the observed blue shift of the experimental optical absorption edge. Moreover, the concentration dependence of the effective mass, which results from the non-parabolicity of the conduction band, agrees well with recent experimental findings [3,4].

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Defects on TiO_2 surfaces*

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Defects strongly affect the physical and chemical properties of metal oxide surfaces. Here we discuss two types of defects commonly found on oxide surfaces, step edges and oxygen vacancies. We report first-principles calculations of the structure, energetics, and chemistry of step edges on the (101) surface of TiO_2 anatase, an important photocatalytic material. A procedure based on systematic calculations of related vicinal anatase TiO_2 surfaces has been used, which yields step edge energies with remarkable accuracy. Oxygen vacancies on TiO_2 surfaces are experimentally found to introduce localized Ti^{3+} $3d^1$ states about 1 eV below the conduction band. These states are not removed when water is dissociatively adsorbed at the vacancy and hydroxyl groups are formed. Calculations based on pure DFT functionals have not been able to satisfactorily reproduce these findings. We show that a correct description of the localized defect states on the reduced and hydroxylated rutile $TiO_2(110)$ surface is achieved only if proper geometry relaxation is accounted for using hybrid exchange functionals.

* Work in collaboration with Xue-Qing Gong, *Department of Chemistry, Princeton University;* Cristiana Di Valentin and Gianfranco Pacchioni, *Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca*; Ulrike Diebold, *Department of Physics, Tulane University.*

First-principles calculations of capacitors at finite bias potential

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When the thickness of an oxide film is reduced to few unit cells, its dielectric properties (which are relevant, e.g., for nonvolatile ferroelectric memories and as gate oxides in MOSFET transistors) start to deviate from those predicted by macroscopic models, and cannot be disentangled from the metallic or semiconducting contacts. One particularly important issue related to interfacial effects is the "dielectric dead layer", which plagues the performance of thin-film perovskite capacitors by substantially reducing the effective permittivity (κ) of the active high-κ material. The microscopic origins of this reduced permittivity, and in particular whether it stems from defects or from the fundamental properties of a metal/insulator interface, are not well understood.

To address this problem from first principles, we will first show how the macroscopic polarization (and the coupling to an external field) can be rigorously defined for a periodic metal-insulator heterostructure, by using techniques and ideas borrowed from Wannier-function theory [1]. We will then demonstrate our new method by calculating the dielectric properties of realistic $SrRuO_3/SrTiO_3/SrRuO_3$ nanocapacitors [2]. In particular, we demonstrate the existence of an intrinsic dielectric dead layer and analyze its origin by extracting the ionic and electronic contributions to the electrostatic screening. We establish a correspondence between the dead layer and the hardening of the collective $SrTiO_3$ zone-center polar modes, and determine the influence of the electrode by repeating our calculations for $Pt/SrTiO_3/Pt$ capacitors. These results provide practical guidelines for minimizing the deleterious effects of the dielectric dead layer in nanoscale devices.

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Self-interaction correction calculations of f-electron materials

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The self-interaction corrected local spin density (SIC-LSD) approximation is reviewed. This scheme allows for a localized description of some of the electronic degrees of freedom, and the self-interaction energy acts as an energy of localization which conquers the energy gained upon band formation. Applications to f-electron materials are discussed with emphasis on systems with competing valencies, notably SmS, TmSe and PuSe. In particular, PuSe is seen as equivalent to SmS under compression. While cohesive properties of localized systems is generally well described by SIC-LSD, other aspects of the electronic structure need further modelling. The atomic-like multiplet structure of the excited states is one prominent example. The photoemission spectra of f-electron compounds are modelled by a dynamical mean field theory. The complete multiplet spectrum of a single ion is calculated by exact diagonalization of the two-body Hamiltonian of the f^n shell, and the ensuing atomic self-energy operator is combined with the LDA Hamiltonian. For PuSe, additional interacttion between the Pu f-shell and the conduction electrons must be incorporated.

Orbital magnetization in periodic solids and its connection to NMR

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A complete description of magnetism in solids requires not only the spin degrees of freedom, but also the "orbital magnetization." Despite the recent surge of interest in magnetic materials, it is quite surprising that the theory of orbital magnetization has remained in a condition similar to that of the polarization before the early 1990s, when the problem of computing finite polarization changes was solved by the introduction of the Berry-phase theory.[1] The essential difficulty, that the matrix elements of the position operator $\mathbf{r}$ are not well-defined in the Bloch representation, could be overcome by reformulating the problem in the Wannier representation. In order to derive an analogous theory for the orbital magnetization, we again work in the Wannier representation and assume a periodic insulator with broken time-reversal symmetry, vanishing (or commensurate) magnetic field, and zero Chern numbers. We show that a naive replacement of the dipole operator $\mathbf{r}$ by the circulation operator $\mathbf{r} \times \mathbf{v}$ in the expectation value of a bulk Wannier function gives only one contribution to the magnetization, i.e., the magnetization associated with the internal circulation of bulk-like Wannier functions. The missing contribution arises from net currents carried by the Wannier functions at the boundary of the sample. We prove that both contributions can be expressed as bulk properties in terms of Bloch functions in a gauge-invariant way.[2,3] With this new formalism at hand, I will then outline a possible approach for computing NMR shielding tensors via the orbital magnetization.

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Quantum mechanics in a comoving frame: an emergence of time-dependent deformation functional theory

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In this talk I introduce a new DFT-like approach to the nonequilibrium quantum many-body problem – a time-dependent deformation functional theory (TDDefFT). One of the main practical motivations to reconsider the basics of conventional time-dependent (current) density functional theory is a so called ultranonlocality problem in nonadiabatic TDDFT. Physically the ultranonlocality is related to a convective motion of the electron fluid: in the nonadiabatic theory the particles at a given point of space retain the memory of their previous positions. As a result the universal density functionals of TDDFT become extremely nonlocal.

The key idea of TDDefFT is to eliminate this source of nonlocality by separating the convective motion, and the motion of quantum particles relatively to the convective flow. Formally this corresponds to the transformation of the exact many-body equations of motion to a comoving Lagrangian frame, i. e. to a local noninertial frame moving with a flow. Within this formalism the convective motion is described by a set of trajectories of infinitesimal fluid elements (the Lagrangian trajectories), while the relative motion is determined by the many-body wave function in the comoving frame. It turns out that the many-body problem in the comoving frame does not contain any external field. The dynamics is completely determined by a fundamental geometric characteristics of the frame – the Green's deformation tensor g_{ij} that plays a role of an effective metric in the Lagrangian space. Hence this many-body problem appears to be universal. It determines the wave function (and thus any observable) as a universal functional of the deformation tensor. In particular, the stress force in the equation of motion for the Lagrangian trajectories, as well as xc potentials in the Kohn-Sham scheme are unique functionals of g_{ij}.

The most interesting property of this approach is that a DFT-like theory emerges in a constructive fashion. It appears as a natural, unavoidable step in solving the quantum many-body problem in a comoving frame. Practically it opens up a possibility to describe nonadiabatic xc effects using local functionals of a new basic variable, the deformation tensor.

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Fast GW calculations using ultra-localized Wannier functions

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We present a novel approach for performing faster first-principles GW calculations in larger systems. A description of the valence and conduction manifolds in terms of ultra-localized non-orthogonal generalized Wannier functions permits to reduce the dimension of the basis set required for describing the space of single electron transitions. This dimension scales linearly with the size of the system. Then a real-space imaginary-time approach is used to calculate the self-energy operator in the space of Kohn-Sham eigenstates. Ultrasoft pseudopotentials are straightforwardly implemented within this scheme. We validate our approach by calculating the vertical ionization energies of selected molecules and find excellent agreement with the experiment. With respect to the calculations performed using the complete matrix of single electron transitions, we observe a speed-up of around two orders of magnitude.

Geometric Phases, Distribution of Electron Charge Centers, Wannier Functions and Bonding in Materials

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We describe a scheme to determine non-abelian geometric phases [1] of Bloch electrons in the frame-work of density functional theory and discuss their use and implications to the theory of polarization and construction of Wannier Functions [1, 2]. Through projection of Wannier functions onto atomic orbitals, we introduce concepts of Bond Orbital Overlap Population and Bond Overlap Position Population. Using these constructs, we show that the origin of anomalously large Born dynamical charges in d^0 transition metal oxides, such as ferroelectrics, is in the long-range transfer of small electronic charge between transition metal ions through the bridging oxygen ion, analogus to double exchange mechanism in ferromagnets [3]. Finally, we present a new gauge invariant functions, Distribution of Electron Charge Centers (DECC) that provides partitioning of extended charge density in crystals, yielding a description of electronic structure in terms of average position of electrons [4]. This provides a natural picture of bonding, with a general and precise definition of an $n-$electron $m-$centre bond.

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* Work done with Joydeep Bhattacharjee and partly with S. Narasimhan.

von NEUMANN LATTICES and WANNIER FUNCTIONS

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Abstract:

In his celebrated book "Mathematical Foundations of Quantum Mechanics," von Neumann introduced the notion of a lattice in the phase plane [1]. This lattice has a unit cell of area h, the Planck constant, and is of wide use both in physics and in signal processing, where it is called the Gabor lattice[2]. One can construct such a phase space lattice by using the elementary shift operators $T(a) = \exp\left(\frac{i}{\hbar}pa\right)$ and $\tau\left(\frac{2\pi}{a}\right) = \exp\left((ix\frac{2\pi}{a}\right)$. These operators commute and they determine the *kq*-representation[3]. The *k* and *q* are the symmetric coordinates for periodic potentials. In solids of much importance are the Wannier functions, which is an orthonormal set of functions on a crystalline lattice in configuration space[4]. They play an important role in the magnetic field problem, where one can assign a von Neumann lattice to each Landau level. In his book [1] von Neumann constructed a set of coherent states on a lattice in phase plane by using the shift operators *T(a)* and $\tau\left(ix\frac{2\pi}{a}\right)$, and stated without proof that the set he had built was complete and that it could be made orthogonal. The completeness part of his statement was first proven about 40 years after the German edition of the von Neumann book[5-7]. The orthogonality part of von Neumann's statement has taken a fascinating turn in the last 25 years, after 1981, when the Balian-Low theorem appeared. According to this theorem it is impossible to build an orthonormal set of functions by shifting a single function on a von Neumann lattice. An idea to bypass the Balian-Low theorem was raised by Wilson and co-worker in a numerical iteration procedure[8]. This procedure was later complemented by an analytic construction by Daubuchies et al.[9].

More recently[10], a symmetry framework was developed for a unique assignment of an orthonormal basis on a von Neumann lattice. This basis can be interpreted as having the meaning of Wannier functions on a phase plane.

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Spin-dependent all-electron tunneling through junctions

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In recent years one is witnessing an increasing experimental effort in preparing junctions made of ferromagnetic leads and a variety of different barrier materials including simple oxides, semiconductors, piezoelectrics, ferroelectrics and multiferroics. The most prominent one is certainly the tunneling magneto-resistant (TMR)-system Fe/MgO/Fe [1], which is the core of a non-volatile memory cell of a magnetic random access memory. Characteristic to all systems is that structural and chemical details at the interface determine substantially the tunneling characteristics, which makes the description of the transport properties a challenging task.

In order to provide an understanding of the transport properties of these systems from an *ab initio* description of the electronic structure, giving account of the complex interplay between the electronic structure, the details of the atomic arrangement and the magnetism in these planar junctions we developed an electronic transport code in the context of an all-electron full-potential scheme. We implemented the Green-function embedding formalism within the framework of the full-potential linearized augmented plane wave (FLAPW) method [2] as implemented in the `FLEUR`-code [3]. This approach allows the calculation of the embedded Green function of the finite scattering region with the correct boundary conditions of attached semi-infinite leads, which appear as additional energy-dependent non-local potentials in the transport calculations.

We focus on results of the Fe/MgO/Fe based system [4, 5], for which we show that very small changes at the interface can have drastic effects on the conductance. If time permits we will present a second system: a $SrRuO_3/SrTiO_3/SrRuO_3$ three-layer junction, where $SrRuO_3$ is a ferromagnetic metal and $SrTiO_3$ forms an insulating barrier. We discuss the role of the interface structure and chemistry on the spin-polarization of the electronic transmission in these systems.

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ABSTRACTS

OF

POSTERS

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Hydrogen dynamics in hydrogenated amorphous silicon

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We report first principles *ab initio* density functional calculations of hydrogen dynamics in hydrogenated amorphous silicon. Thermal motion of the host Si atoms drives H diffusion, as we demonstrate by direct simulation and explain with simple models. Si-Si bond centers and Si ring centers are local energy minima as expected. We also describe a new mechanism for breaking Si-H bonds to release free atomic H into the network. We find that H_2 diffuses rapidly, suggesting that molecular forms of hydrogen may also be important to understanding H motion, in a-Si:H in agreement with recent conjectures. H dynamics in a-Si:H is dominated by structural fluctuations intrinsic to the amorphous phase not present in the crystal.

Full first-principles simulations on 180° ferroelectric stripe domains in realistic ferroelectric capacitors.

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The field of ferroelectric thin films is at a momentous stage. Several experimental and theoretical works, both within a phenomenological approach and atomistic models, have been devoted to ascertain the phase diagrams of epitaxial ferroelectric thin films, as a function of the thickness, composition, temperature and strain [1].

The main reason for the poor understanding of some of the size-effects on ferroelectricity is the vast amount of different effects that compete and might modify the delicate balance between the long-range dipole-dipole electrostatic interactions and the short-range forces, whose subtle equilibrium is known to be the origin of the ferroelectric instability. Particularly important is the influence of the mechanical and electrical boundary conditions. One the one hand, the strain effects impossed by the substrate might stabilize phases that are not the most stable at the bulk level [2]. On the other hand, unless a perfect screening is provided by free charges in the electrodes[3], the residual depolarizing field tends to supress the latter [4]. In the case of imperfect screening and in order to reduce the electrostatic energy associated with the depolarizing field, two typical mechanisms are observed: (i) the break down of the system into 180° stripe domains and (ii) a uniform progressive reduction of the polarization.

Experimentally, high quality epitaxially plane thin films have been grown. Using synchrotron x-ray scattering, 180° stripe domains have been observed in $PbTiO_3$ grown on $SrTiO_3$ substrate, down to a thickness of 3 unit cells [5, 6]. The same structure has been postulated to explain the thickness-dependence of the tetragonality, switchable polarization and piezoelectric response of $Pb(Zr_{0.2}Ti_{0.8})O_3$ grown on a $SrRuO_3/SrTiO_3$ substrate [7]. In contrast, when $PbTiO_3$ is grown on a metallic substrate ($SrRuO_3$), a monodomain polarization is observed [8]. Thus, there exists still a conundrum, particulary in epitaxial ultrathin heterostructures, as to how the lattice and polarization properties scale with thickness for different ferroelectric compositions.

First-principles simulations are a valuable tool to understand the microscopic behaviour of the heterostructures. Most of the works have been done using a first-principles based model Hamiltonian approach [9, 10]. Depending on the degrees of screening and epitaxial strain constraint, a rich variety of patterns for the polarization are found, including an exotic vortex structure. Here, using a full first-principles density-functional-theory approach we have simulated 180° ferroelectric stripe domains at 0 K in $SrRuO_3/BaTiO_3/SrRuO_3$ and $SrRuO_3/PbTiO_3/SrRuO_3$ realistic ferroelectric capacitors epitaxially grown on a $SrTiO_3$ substrate. For a ferroelectic thin-film 2 unit cells thick, the lateral sizes of the domains ranged from 2 to 4 unit cells. Very accurate calculations are required since the relevant differences of energies between the phases are much smaller than the absolute value of the energy for a typical supercell. Therefore, a cutoff of 400 Ry for the real-space grid integrations and a 12 × 12 × 1 Monkhorst-Pack grid for the sampling in $\boldsymbol{k}$-space were used. Despite this huge computational effort, the calculations were affordable due to the efficiency of the parallel version of SIESTA [11]. The vortex structure is reproduced as the most stable phase in all the configurations. This vortex is closed by a TiO_2 chain and by the metal atoms in the first metallic layer, suggesting the posibility of an ionic polarizability of conductive metal oxides [12]. The in-plane displacement of the atoms is essential to stabilize the domain structure. If the in-plane coordinates of all the atoms are constrained to the square geometry imposed by the $SrTiO_3$ substrate, the paraelectric configuration is the most stable phase (no vortices), suggesting a possible explanation for the different behaviour observed in the heterostructures grown experimentally.

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Absolute rate of thermal desorption from first-principles simulation

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Abstract

We present a technique for computing by first-principles simulation the absolute desorption rate γ of adsorbate molecules from a surface for any coverage and temperature. The technique is valid when the thermal equilibration rate on the surface is faster than γ, and is based on an exact expression for γ in terms of the difference of non-configurational chemical potentials of gas-phase and adsorbed molecules. This difference is expressed in terms of a potential of mean force, which is computed by constrained first-principles molecular dynamics. At the time of writing nuclear quantum effects are being fully included using first principles path integral techniques. The technique is applied to D_2O on the MgO (001) surface at low coverage, using the generalised gradient approximation (GGA) for exchange-correlation energy. Comparisons with experimental TPD data allow an assessment of the accuracy of GGA for the adsorption of D_2O on MgO (001).

First principles growth of gold nanowires with impurities

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We present a complete study of the formation of gold nanowires paying special attention to the role of different impurities (H, C, O, S) in the arrangement of the atoms and the electronic structure properties of the chains. The whole process of the simulation is considered, so we start from an amorphous structure and stretch it until the chain is formed. The stretching is performed using ab initio molecular dynamics. During the early stages of the stretching the hydrogen evaporates, so it can be ruled out as a contaminant. Carbon and oxygen have a low probability (10%) of participating in the chain while sulphur atoms almost always participate as they have a probability of 92%. There are experimental evidences of extremely long distances (up to 5 Å) between two consecutive gold atoms of the chain. We conclude that carbon and sulphur impurities "glue" these gold atoms together and stabilize the chain.

Density-Functional treatment of nanosystems : decreasing the number of self-consistent field cycles

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The number of self-consistent cycles needed for Density Functional Theory treatment of metallic systems diverges as the size of the unit cell, if such calculation does not include an adequate preconditioner (e.g. Kerker's technique). We show that when the system is inhomogeneous, and only partly metallic (e.g. metal slab in vacuum, of increasing size ; nanosystems), Kerker's technique does not improve the convergence with cell size. Moreover, even Ho's *et al.* Newton-Raphson technique do not work. By contrast, the use of the dielectric matrix within the Random Phase Approximation leads to a large convergence improvement. However, such a matrix is rather expensive to compute ($O(N^4)$), so this method is impractical for very large systems. We present a new preconditioning approach which might be suitable for large-scale metallic nanosystem studies. Based on a generalization and reformulation of Kerker's preconditioner, this simple real-space algorithm can be used for space-parallelized systems where the coulombic response is a foremost problem to reach true linear scaling of Density Functional Theory computations.

Structure and electronic structure of the (001) surface of half-metallic manganites

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The high spin polarization of the conduction charge carriers in mixed-valence manganites has stimulated considerable interest for their potential application as spin injection contacts in spintronic devices. A good understanding of the surface and interface properties is highly desirable for future applications. The unusual physical properties of these perovskites are frequently discussed in the framework of the double-exchange model in the cubic structure. Recent experimental and theoretical works reveal the importance for the electronic structure of the lattice distortions and oxygen vacancies possibly present in the surface, whose effect on the surface magnetic properties are unknown. We present results for a fully relaxed (001) surface in optimally doped half-metallic manganites ($La_{0.7}Sr_{0.3}MnO_3$), based in density functional calculations, with explicit doping and in the distorted orthorhombic phase. The theoretical bulk band dispersions are compared with recent ARPES experiments. The crystal termination at the surface gives rise to a splitting of the degenerate t_{2g} and e_g levels, and a surface state with $d_{z2}+d_{xy}$ character is formed. The calculations for the relaxed structure show that the tilting of MnO_6 octahedra is reduced near the surface, and there is a buckling, with Mn off-centring as Ti in $BaTiO_3$, that decreases rapidly inside the material. As a result, the surface state shifts to lower energies, although still very localized in the first layer. The Mn off-centring favours the occupation of the conduction d_{z2} states, which become more localized. The role of oxygen vacancies in the surface electronic structure is also explored.

Adsorption of Organic Pollutants on Mineral Surfaces: DFT calculations of Poly-chlorinated Aromatic Hydrocarbons on Clays and Carbonate Minerals

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Poly-chlorinated biphenyls and dibenzo dioxins are persistent, toxic pollutants that have been released into the environment by human activity. In order to understand their distribution in the environment, and to remediate affected areas, it is of utmost importance that their behaviour is properly understood at the molecular level, especially with respect to their adsorption onto the minerals with which they usually come into contact.

Density functional theory calculations have been carried out, using the SIESTA code, on a number of systems comprising PCBs, PCDDs and mineral surfaces. The surfaces reported here are the pyrophyllite ($AlSi_2O_5OH$) (001) surface, the calcite (211) surface, and the (001) surface of a smectite of the formula ($Na(Al_3Mg)Si_8O_{20}(OH)_4$), which presents exposed Na^+ cations to the complexing species.

In some cases, suites of over 100 calculations have been generated which ‘scan’ the pollutant molecule across the surface to gain an energy profile and find the most likely place for adsorption. These, along with the optimisation calculations, provide information that will be used to fit empirical potentials for the systems, so that their behaviour can be studied at a larger scale.

Title: Ice systems in our atmosphere
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Addressing the enviromental challenges via first principle calculations is one of the most interesting and new subject of numerical simulations. The chemical reactions which take place on the the surface of the ice particles which compose polar stratospheric clouds, are very important in the atmospheric science since they determine, for example, the ozone depletion [1]. These reactions are known to be enhanced by the presence of electrons generated by cosmic rays. Via ab-initio Molecular Dynamics using the QuantumEspresso code, we have found that the excess electron on an (0001) ice surface, at finite temperature $T \sim 150K$, preferentially stays in a surface state, at least up to a few ps, inducing a complete rearrangement of the uppermost bilayer, in order to increase the number of dangling-OH bonds pointing outside the surface. This transformation does not take place on the neutral (0001)-surface, in the same temperature conditions [2]. Moreover, we show that the CCl_4, one of the most common chlorocompounds in atmosphere, dissociates easily on the reconstructued ice surface while it remains stable on the unreconstructed one [3].

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Hydrogen bonding in adenine-thymine DNA base pair: Anharmonic effects in intermolecular and intramolecular H-bond vibrations

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The equilibrium structures, binding energies, vibrational harmonic frequencies and their anharmonic corrections of the adenine-thymine DNA base pair system have been studied using the second-order Møller-Plesset perturbation theory (MP2) and different (B3LYP, BHandHLYP and BHLYP) functionals at DFT levels of theory, considering the D95V and D95V++** basis sets. The widely used *a posteriori* Boys-Bernardi "counterpoise" (CP) correction scheme for basis set superposition error (BSSE) elimination, implemented in GAUSSIAN03 program package, has been included in our calculations in order to take into account the BSSE effects in geometry optimization, binding energies and different approximation of the vibrational frequencies. The results obtained by *ab initio* MP2 method are compared with those calculated considering different exchange-correlation DFT functionals and the usability of the chosen DFT functionals in the adequate description of intermolecular hydrogen bonds are discussed. The effects of the sugar group on the DNA base normal mode vibrations are also presented.

First principles calculations of the structural and elastic properties of LiCdP and LiCdAs

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Abstract: We have investigated the structural and elastic properties of the Nowotny-Juza filled tetrahedral compounds LiCdP and LiCdAs by using the full-potential linearized augmented plane wave method within the local density approximation. The α-phase for both materials, which is energetically favourable than the β one, is softer than the binary analogous compounds; InP and InAs. The calculated sound speeds are quantitatively similar for the ternaries and their binary analogous compounds.

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Electron-phonon coupling in halogen-doped carbon clathrates

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Superconductivity at $T_c \sim 4$ K has been recently reported for boron-doped diamond synthesized at high pressure and temperature ($P \sim 10$ GPa and $T = 2500 - 2800$ K). *Ab-initio* calculations have shown that metallization in this system is produced by hole injection into the intrinsic diamond valence bands, as later confirmed by angle resolved photoemission measurements. The possibility to tune T_c in diamond by changing the carrier concentration in its intrinsic bands, either by *p*-type or *n*-type doping is thus intriguing and acquired a new boost from this recent discovery. In this work, based on *ab-initio* calculations, we investigate carbon clatrathes as an alternative tetrahedral form of carbon suitable to turn metallic upon doping. Electronic structure and electron-phonon coupling of carbon clathrates C_{40} , C_{34} and C_{46} doped with interstitial halogen atoms (fluorine, iodine) in the fullerenic cages of the host, have been investigated within density functional linear response theory. It turns out that, while in C_{40} and C_{46} the halogen is only partially reduced, in FC_{34} an electron is transferred to the guest ion by injecting holes in the valence band of the host. The calculated electron-phonon coupling constant is as large as $\lambda=0.85$. We propose that halogen-doped carbon clathrates might represent another form of tetrahedral carbon, besides the recently found B-doped diamond, suitable to turn superconductive at high temperature ($T_c \sim 77$ K from McMillan formula with $\mu^*=0.1$).

Comparative study of the properties of $BaTiO_3$ and $PbTiO_3$ using DFT (LDA, GGA), HF and hybrid (B3LYP) functionals

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The study of ferroelectrics (FE) requires to be able to reproduce accurately not only the structure (lattice constant, tetragonality c/a and atomic distortions) but also in some cases such as determination of optical properties and characterization of metal/FE interfaces, their energy gap E_g. DFT underestimates E_g of a typical FE by a factor of about two while hybrid Hartree Fock (HF)-DFT functionals such as B3LYP are known to give improved values for E_g. Therefore, we performed B3LYP and HF study of $BaTiO_3$ and $PbTiO_3$ and compared our results to those of LDA and GGA. For the cubic phase, B3LYP gives very good agreement with the experimental lattice constants and E_g. For the tetragonal FE phase, if the atomic positions are relaxed at the experimental lattice constants then LDA, GGA and B3LYP give comparable results for the atomic distortions. However, full relaxation of the tetragonal phase using B3LYP gives a supertetragonality comparable to GGA. We performed hybrid calculations for different values of the three Becke's parameters and found that the supertetragonality is introduced by the non-local part of the Becke GGA exchange. This suggests that a hybrid functional generated from a better GGA[1] might provide simultaneously better structural and electronic properties of FE.

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Ab initio electronic and transport properties of a hybrid Si/organic/Si interface from Maximally Localized Wannier Functions

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The last years have witnessed a growing interest in the study of electronic and transport properties of a new class of nanostructured devices constituted of hybrid molecular/semiconductor interfaces. The link between the well established silicon technology and state-of-the-art methods of surface functionalization is expected to lead to novel nanostructured materials, with tunable electronic and transport characteristics.

Here, we theoretically investigated the electronic and transport properties of a hybrid silicon/molecule/silicon interface, constituted of two semi-infinite silicon bulk leads and the conductor region given by a monolayer of di-hydroxybiphenyl molecules ($C_{12}H_{10}O_2$).

The electronic structure is calculated from a plane-waves pseudopotential implementation of the Density Functional Theory, and the coherent transport properties are evaluated within the Landauer approach properly extended to 3D systems.

We analyzed the electronic structure in terms of surface-molecule and molecule-molecule interactions, observing a re-hybridization of the molecular orbitals with the continuum of states of the Si-substrate and the broadening of the original molecular π peaks in the density of states, due to the phenyl-phenyl coupling. We didn't observe, anyway, the modification of the band-like properties (e.g. the bandgap) of the Si(111) surface near the Fermi level.

We directly evaluated the electron transport across the Si-molecule-Si interface, in terms of quantum conductance, using a recently developed *ab intio* methodology, based on the calculation of the maximally localized Wannier Functions and implemented in the WanT suite of codes.

First-principles study of $PbTiO_3/SrTiO_3$ multilayers

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Nowadays, ferroelectric oxide superlattices present a considerable interest since they constitute artificial materials with potentially enhanced physical properties. The combination of $PbTiO_3$ and $SrTiO_3$ has been studied experimentally and an unusual increase of the ferroelectric polarization has been measured for the smallest $PbTiO_3$ thicknesses [1]. This surprising recovery of ferroelectricity cannot been explained by simple electrostatic considerations.

In this work we study from first-principles $(PbTiO_3)_n/(SrTiO_3)_m$ superlattices focussing mainly on the $(PbTiO_3)_1/(SrTiO_3)_1$ case. We demonstrate the existence of an unexpected coupling between out of plane ferroelectric distortion (FE) and the antiferrodistortive motion (AFD) of the oxygens. This never previously reported FE/AFD coupling yields significant increase of the polarization of the system and might explain the experimentally observed recovery of ferroelectricity.

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Recent progress with the linear scaling code, CONQUEST

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We will present details of recent developments and applications of the linear scaling code, CONQUEST[1,2], which is capable of being run at a variety of different levels from ab initio tight binding up to full DFT with plane-wave accuracy[1]. The electronic structure of the system is found in terms of support functions (localised functions centred on atoms, represented in terms of basis functions[3]) and the density matrix in this representation. The search for the ground state is divided into three stages: first, the density matrix; second, self-consistency between charge and potential; third, the form of the support functions in terms of the basis functions. Details of basis sets[3], forces[4] and recent applications to problems including Ge "hut" clusters on Si(001) will be given[2], along with information about the general release of the code.

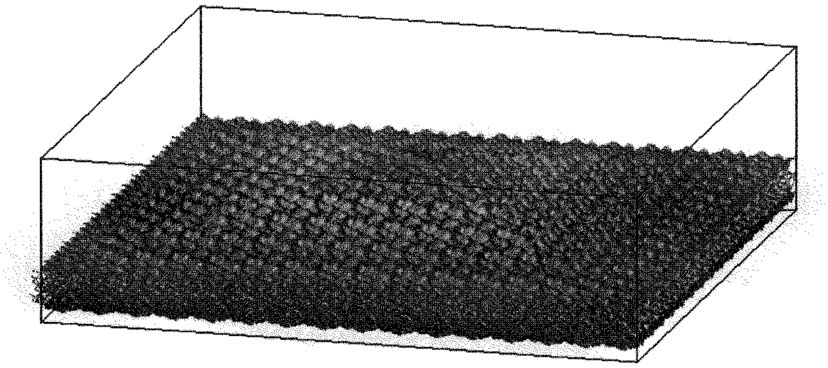

Figure 1: Charge density from a Ge hut cluster on Si(001); colour indicates height

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"A DFT study of low index polar surfaces: the case of SiC and ZnO"

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With the advent of nanostructured devices, it appears evident that the role of surface and interface effects may prevail on bulk properties and determine the physical characteristics of the material at the nanoscale: in particular, the understanding of the electronic properties of nanosized structures demands for a proper accurate treatment. Here we report on first principles density functional calculations of the structural and electronic properties of the so called "non-polar" low index surfaces of hexagonal silicon carbide (SiC) and zinc oxide (ZnO), specifically focussing on surface polarity. We first provide an accurate analysis of the macroscopic polarization field as a function of the hexagonality and ionicity of the compound, and than describe in details the properties of the relaxed surfaces. Our predictions nicely compare with recent experimental data on similar SiC and ZnO surfaces: in particular we obtain good agreement between the perpendicular surface dipole component and the experimental work functions values. Moreover, for the first time, we highlight the presence of a strong in-plane dipole component related to dangling bond rearrangement at the surface, which opposes the bulk spontaneous polarization. The decaying behaviour of this dipole inside the slab shows that the presence of surfaces deeply change the polar properties of structures of few nanometers size, while bulk polarization is recovered for thicker systems. Given the importance of surface dipoles in adsorption and functionalization processes, we finally analyze the local surface electric field by employing a simple polar model molecule (HF) as a probe: we describe the interaction in terms of the potential energy surface (PES) experienced by the molecule. This allows us to give a complete description of the surface polarity and to draw conclusions on the most likely adsorption sites of charged and polar species.

Metallicity in individual MMX chains

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We present an *ab initio* study of the structural and electronic properties of the isolated halogen-bridged MMX polymer $[Pt_2(CH_3CS_2)_4I]_n$ and of various possible modifications of its sequence, in the framework of density functional theory. The computed bandstructure of the infinite regular polymer reveals a net metallic character: this evidence is compatible with the outcome of recent measurements done in the solid phase at room temperature. Taking the regular $[Pt_2(CH_3CS_2)_4I]_n$ polymer as our reference system, we analyze the origin and the robustness of the metallic state along the chain, with respect to a large set of geometrical and chemical perturbations of the subunits. In particular, we considered partial substitutions of the metal, halide and dithiocarboxylate ligand subunits, as well as structural strain, defects and magnetic effects. Our results demonstrate that the metallic character of single MMX chains is very resistant to a wide range of possible distortions.

New oxynitride perovskites with huge polarizations

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Based on first-principles calculations we predict the existence of stable ordered oxynitride perovskites. Their structures are derived from the perovskite structure by the replacement of one oxygen atom by one nitrogen atom and the divalent cation with a trivalent cation in each unit cell. These compounds have polar structures with P4mm symmetry. We try different combinations of trivalent and tetravalent cations and find that $YSiO_2N$ and $YGeO_2N$ are dynamically stable polar insulators. They show giant effective spontaneous polarizations: 130 μC/cm2 for $YSiO_2N$ and P=103 μC/cm2 for $YGeO_2N$ as obtained from Berry phase calcualtions. These are the largest polarizations known so far. They present also interesting piezoelectric and non-linear optical properties. With such outstanding properties they are promising materials for a large range of applications.

Optical properties of real surfaces: local field effects at oxidized Si(100)(2x2) computed with an efficient numerical scheme

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We show the application of an efficient numerical scheme to obtain the independent-particle dynamic polarizability matrix $\chi^{(0)}(\mathbf{r}, \mathbf{r}', \omega)$, key quantity in modern *ab initio* excited state calculations. The method has been applied to the study of the optical response of a realistic oxidized silicon surface, including the effects of local fields. The latter are shown to substantially increase the surface optical anisotropy in the energy range below the bulk bandgap. Our implementation in a large-scale *ab initio* computational code allows us to make a quantitative study of the CPU time scaling with respect to the system size, and demonstrates the real potential of the method for the study of excited states in large systems.

Ab-Initio study of elastic properties of single and polycrystals of TiO_2, ZrO_2, HfO_2 in high pressure phases

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In this work we combine the elasticity theory together with quantum-mechanics simulations to find the elastic properties corresponding to the cotunnite high-pressure phase of the group IV-B oxides: titania, zirconia and hafnia. By means of the self-consistent SIESTA code which utilize pseudopotentials, density functional theory in the local approximation (LDA) and a local base of atomic orbitals, the six components of the stress tensor are calculated by the application of uniaxial, biaxial and shear deformations. From the stress - strain relationship $\vec{\sigma}=\hat{C}\cdot\vec{e}$, the C_{ij} components of the elastic constants tensor were calculated. From these C_{ij} constants and using Voigt and Reuss theories, the bulk, Young, shear moduli as well as Poisson coefficients were determined. Some thermo-acoustic properties like the speeds of propagation of transverse, longitudinal sound waves and Debye temperatures were also estimated. We have found that in hafnia and circonia, the elastic constants C_{11}, C_{22} and C_{33} are increased notably regarding the experimental values of the monoclinic phase $P2_1/c$, similar situation to what happens to titania if the constants are compared with its normal phase, rutile. Shear elastic constants C_{44}, C_{55} *and* C_{66} show in all oxides, nearer values to those found in the corresponding normal phases. In the case of the cotunnite TiO_2, phase known as the hardest oxide, elastic constants were also calculated with the GGA approach.

First Principles Study of Ground State Properties of InN

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We present a detailed theoretical study of the ground state properties of bulk InN as obtained by state of the art DFT calculations [1]. InN is deserving a renewed interest in electronic and specifically in photovoltaic applications because of its electronic features, such as a direct band gap of about 0.7 eV and an absorption coefficient of 7×103 cm-1 at 0.75 eV, that render it extremely promising as a collector for electrons from a solar radiation absorber. We have developed a well performing In Ultra-Soft Pseudopotential that explicitly includes semicore d-states, and with the PBE exchange-correlation approximation. Beyond simple molecular systems, we test the pseudopotential by studying the electronic and vibrational properties of bulk InN in the Zincblende and Wurtzite structures, providing also values for the spontaneous polarization, the effective charges and the piezoelectric tensor.

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Ab initio Melting Curve of Molybdenum by the Phase Coexistence Method

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Abstract

Ab initio calculations of the melting properties of molybdenum in the 0-400 GPa pressure range are presented. Results are obtained with the projector augmented wave (PAW) implementation of density functional theory and generalized gradient approximation for the exchange-correlation energy. We prove the reliability of our approach by carrying out several zero-temperature tests in which we assess excellent agreement with the full-potential linearized augmented plane wave method (FP-LAPW) and experiments. Special attention is paid to the description of the electronic properties of the system at equilibrium and under high compression as well. The *ab initio* melting curve is worked out in two stages: initially, a melting curve is obtained by means of the phase coexistence method and embedded-atom potential model, subsequently, corrections which explicitly account for the differences between the Gibbs free energy of the model and *ab initio* systems are applied to it. We find excellent agreement with experimental zero-pressure data and high-pressure shock-wave measurement, however, huge discrepancies with respect to diamond-anvil cell results are encountered. The changes of electronic structure on melting are analyzed and found, contrary to what has been suggested recently, rather small.

Study of the small-q contribution to the polarizability and the intraband term: from jellium to the periodic solid.

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The computation of the GW correction for a bulk jellium shows the importance of considering the intraband contribution in the **q**->0 limit for the polarizability, since its absence induces the appearance of a spurious gap in metallic systems. To include intraband contributions to the polarizability we propose an approach not requiring Fermi-surface integration, which would have a heavy numerical load. The approach we propose is based on determining the limiting behaviour of the polarizability by a fit of its Taylor expansion in the region where **q** is small but finite. This computational approach has fewer numerical problems in evaluating the intraband contribution. In this way we extend the jellium case, where the RPA polarizability is known analitically (the Lindhard function), to real solids. We calculate the GW corrections for real metals such Na and Al.

Orbital magnetization in a supercell framework: Single k-point formula

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The position operator **r** is ill-defined within periodic boundary conditions: owing to this, both the macroscopic (electric) polarization and the macroscopic orbital magnetization are nontrivial quantities. While the former has been successfully tamed since the early 1990s, the latter remained a long-standing unsolved problem. A successful formula within DFT for crystalline systems has been recently found. [1] The formula is based on a Brillouin-zone integration, which is discretized on a reciprocal-space mesh for numerical implementation. We find here the single **k**-point limit, useful for large enough supercells, and particularly in the framework of Car-Parrinello simulations for noncrystalline systems. We validate our formula on the test case of a crystalline system, where the supercell is chosen as a large multiple of the elementary cell. Rather counterintuitively, even the Chern number (in 2d) can be evaluated using a single **k**-point diagonalization.

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Pseudo Jahn-Teller effect in perovskite oxides: as a origin of ferroelectricity

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Abstract

We investigate the electronic structure and ferroelectric lattice instability of two classical ferroelectric perovskites $PbTiO_3$ and $BaTiO_3$, though first-principles pseudopotential total energy calculations. We demonstrate how the pseudo Jahn-Teller effect drives the ferroelectric phase transition through the interaction between the empty Ti 3d states and the occupied O 2p states. The calculational results indicate that the interaction at the zone-center is predicted to contribute most significantly to the ferroelectric lattice instability.

Theoretical investigation of Palladium-Catalyzed reactions for the selective aerobic oxidation of organic molecules

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Significant recent progress in the use of palladium catalysts for selective aerobic oxidation has emphasized the importance of developing a thorough comprehension of reactions of palladium complexes with O_2. A DFT study of the mechanistic details of the insertion of molecular oxygen into a palladium(II) hydride bond to form a Pd(II) hydroperoxide was carried out. Also we are trying to establish whether this formal dioxygen-insertion reaction proceeds by a direct or stepwise mechanism. In particular, the results of this work will be useful to assess the involvement of Pd(0) intermediates. Calculation carried out until now show that both the hypothesized mechanisms of direct insertion and, alternatively, coordination followed by migratory insertion are operative, but involve different spin states triplet and singlet respectively.(1)

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Ab initio simulations of alkyl-terminated Si(001) surfaces.

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Self assembled monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface. The interest in the area of self-assembly, and specifically in SAMs, stems partially from their perceived relevance to science and technology. In contrast to ultrathin films made by, for example, chemical vapour deposition, SAMs are highly ordered and oriented and can incorporate a wide range of groups both in the molecular chain and at the chain termination. Therefore, a variety of surfaces with specific interactions can be produced with fine chemical control. In particular, SAM are used in cantilever based detection, as the first step towards the realization of surfaces with specific sensing properties. Understanding how the surface stress and the mechanical properties of a cantilever change upon functionalization is fundamental to achieve accurate quantitative analysis.

Here we present *ab initio* simulations of SAM formation on Si(001) surface to make contact with some recent experimental results [1], in which well packed and ordered alkyl-terminated silicon surfaces were obtained. We will show how the Si(001) surface stress and its mechanical properties (elastic constants) change when organic molecules are attached to it. In particular we will discuss the effect of increasing the surface coverage and the length of the alkyl chain used for the functionalization process. [1] Cerofolini G. F. *Semicond. Sci. Technol.* **18**, 423-429 (2003).

Ab-initio ballistic conductance with spin-orbit coupling

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Ballistic conductance ab initio calculations in heavy metal break junctions require a very accurate description of the nanocontact electronic structure near the Fermi level, in turn quite sensitive to relativistic effects and particularly to spin-orbit coupling. The complex k-vector approach proposed by Choi and Ihm [1] for calculating the ballistic conductance of open quantum systems within the Landauer-Büttiker approach is generalized to fully relativistic ultrasoft pseudo-potentials [2] in order to deal with ballistic transport in presence of spin-orbit coupling. As test cases we present the complex k-vector electronic structure of a perfect monatomic Pt wire, and the ballistic conductance of a Pt wire with an idealized nanocontact consisting of a single strained bond. [3] In these cases we compare the fully relativistic and the scalar relativistic results, highlighting the net effect of spin orbit.

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Time-Dependent DFT investigations of dye-sensitized TiO_2 nanoparticles for solar cells applications

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A key process in the operation of dye-sensitized photovoltaic solar cells is the charge injection from the dye to the semi-conductor. This can either involve photoexcitation to a dye excited state followed by electron transfer to the semiconductor conduction band[1a] or a direct photoexcitation from the dye to the nanoparticle.[1b] We present Car-Parrinello and TDDFT calculations of the absorption spectrum of the prototype $[Ru(dcbpyH_2)_2(NCS)_2]$ and $[Fe(CN)_6]^{4-}$ systems adsorbed on a TiO_2 anatase nanoparticle. We describe the electronic structure and the character of the states involved in the charge transfer process. We show that a direct charge injection takes place in $[Fe(CN)_6]^{4-}$,[2a] at variance with the $[Ru(dcbpyH_2)_2(NCS)_2]$ where electron injection takes place via an indirect mechanism.[2b]

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First Principles Calculation of Materials for Nanoelectronic Devices

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In the last years material scientists and semiconductor industries have put considerable effort into the study of high- dielectric oxides needed to substitute SiO2 in ultra-scaled nano-electronic devices. One of the most promising materials is hafnium dioxide, which at ambient condition presents several metastable structures with different dielectric constants. For this reason the knowledge of the thermodynamics properties of this material and of its phase diagram has a great technological interest. Also titanium dioxide (Ti is in the same column as Hf in the periodic table) presents polymorphism at ambient condition, and it is intensively studied for its technological applications, e.g. photochemical solar cell and optoelectronic devices.

We have computed by plane wave pseudopotentials techniques the structural and the vibrational properties of different HfO2 and TiO2 crystal structures. After structural optimization we compute high- and low-frequency dielectric constant, the Born effective charges, that are necessary to simulate by first principle the infra-red spectra. Further we present some preliminary results of thermodynamics, as the Helmholtz free energy of different phases to investigate their thermal stability.

The Challenge of Approximating Energy Density Functionals: New Theoretical Perspectives

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The undisputed success of Density Functional Theory has been and still is a stimulating ground for the continuous development of theoretical techniques to describe energy functional of the electron density. Here we present different approaches to write and interpret energy functionals , alternative to the standard ones, which combine mathematical rigorous prescriptions and physical well founded arguments. The use of Witten deformation and a variational approach to dequantization allows us to interpret the kinetic functional in terms of stochastic fluctuations; this latter is linked to Nelson theory of quantum fluctuations and in turn can be connected to a reformulation of Levy-constrained search principle in terms of minimization of the correlation functional with respect to the electron conditional probability density. Finally, the possibility to apply such results in realistic calculations is also discussed.

MODELING ADSORPTION OF CO_2 ON Ni (110) SURFACE

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CO_2 adsorption on Ni(110) surface is simulated within the framework of ab-initio pseudopotential density functional theory. Results based on both local spin density (LSDA) and generalized gradient correction (GGA) are discussed..

Beyond possible adsorbed geometries with C_{2v} symmetry, suggested by analogy with the formate adsorption, we found and analyzed a more stable adsorption geometry with no particular symmetry. The existence of a physisorbed state is suggested by findings concerning some stable geometries with small adsorption energy. Common features of all the chemiadsorbed geometries are: (i) non-negligible electronic charge transfers from the metal to the molecule ranging from 0.5 to 0.9 electrons, (ii) bending of the molecule with C atom closest to the surface; (iii) reduction of surface Ni magnetic moment compared to the clean surface (where it is enhanced with respect to the bulk). The energy barrier from physisorption to the most stable chemisorbed geometry is found 0.4eV. Alternative adsorption paths through less favourite, more symmetric chemisorption geometries are possible with barriers less than 0.2eV.

It is found experimentally that CO_2 adsorption increases the workfunction. Our calculations for various coverages agree well with the experimental data. Two contributions, charge transfer and dipole moment of the bent CO_2, are discussed in detail to give a rationale.

Preliminar results for calculated vibrational are presented and compared with the available experimental data as a further indication concerning the best candidates for adsorption geometries.

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Nature of impurity states in N-doped TiO_2

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Titanium dioxide, in the form of powders, films or nanoparticles, is considered an almost ideal material for environmental photocatalysis. However, due its large band gap (3.0-3.2 eV), TiO_2 absorbs only a small portion of the solar spectrum in the UV region. As a shift of the TiO_2 absorption to the visible region would result in a tremendous improvement of its photocatalytic efficiency, a lot of work has been devoted to the attempt of reducing the gap, for example by doping with metal and non-metal atoms. In particular N-and C-doped TiO_2, seem to be very promising. In this work we present and discuss various models of the N-doped systems and the modifications introduced by the dopant in the electronic structure of the material, from DFT calculations [1]. In particular, it is found that N-doping gives rise to localized states in the band gap of the oxide, just above the top of the valence band. Also we analyze the relative stability of the various species as a function of the oxygen chemical potential and discuss the interplay between N-impurities and oxygen vacancies and their crucial role in the processes occurring under visible light irradiation, in relation with recent decisive experimental results based on EPR spectroscopy by the group of Prof. E. Giamello.

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Realistic description of TTF-TCNQ using massively parallel exact diagonalization

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The photoemission spectrum of the quasi one-dimensional organic metal TTF-TCNQ can be described qualitatively using a t-U Hubbard model. For such calculations we have developed a parallel Lanczos code which runs efficiently on modern massively parallel supercomputers like JUBL, Jülich's new BlueGene/L system. To overcome the limitations of the finite system-size we employ cluster perturbation theory (CPT), giving us access to the angular-resolved spectral function with high resolution. As a result, we can resolve the spin-charge separation. Moreover, we compute the total energy of the system by using the Galitskii-Migdal theorem.

Experiments and theoretical estimates for TTF-TCNQ suggest a value for the hopping parameter t. The parameter needed to fit the experiment is, however, larger by a factor of two. We resolve this problem by including realistic values for the next-neighbor interaction V into the model. The effect of this longer-range Coulomb interaction is to broaden the spectrum – very similar to increasing the value of t. This explains why the ad-hoc doubling of t yields a good comparison with experiment. Moreover, we find that the effect of V can be understood already in first-order perturbation theory.

The transport properties of alkanes and π-bonded molecules: the issue of cooperativity.

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The transport properties of alkanes and π-bonded molecules inserted between gold electrodes are investigated using first-principles calculations. This study relies on the use of nonequilibrium Green's functions and the density functional theory, as implemented in the Smeagol [1]. Transmission functions and I-V curves are reported for various molecular junctions and for various surface density. A special attention is devoted to the study of cooperativity in these systems.

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Poster 1

Transition Metal-Ethylene Complexes as High-Capacity Hydrogen Storage Media

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From first-principles calculations, we predict that a single ethylene molecule can form a stable complex with two transition metals (TM) such as Ti. The resulting TM-ethylene complex then absorbs up to ten hydrogen molecules, reaching to gravimetric storage capacity of *»*14 wt%. Dimerization, polymerizations and incorporation of the TM-ethylene complexes in nanoporous carbon materials have been also discussed. Our results are quite remarkable and open a new approach to high-capacity hydrogen storage materials discovery.

Reference : E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, Phys. Rev. Lett (accepted).

Poster 2

Spin-dependent electronic structure of transition-metal atomic chains adsorbed on single-wall carbon nanotubes

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We present a systematic study of the electronic and magnetic properties of transition-metal (TM) atomic chains adsorbed on the zigzag single-wall carbon nanotubes (SWNTs). We considered the adsorption on the external and internal wall of SWNT and examined the effect of the TM coverage and geometry on the binding energy and the spin polarization at the Fermi level. All those adsorbed chains studied have ferromagnetic ground state, but only their specific types and geometries demonstrated high spin polarization near the Fermi level. Their magnetic moment and binding energy in the ground state display interesting variation with the number of *d* electrons of the TM atom. We also show that specific chains of transition-metal atoms adsorbed on a SWNT can lead to semiconducting properties for the minority spin bands, but semimetallic for the majority spin bands. Spin polarization is maintained even when the underlying SWNT is subjected to high radial strain. Spin-dependent electronic structure becomes discretized when TM atoms are adsorbed on finite segments of SWNTs. Once coupled with nonmagnetic metal electrodes, these magnetic needles or nanomagnets can perform as spin-dependent resonant tunneling devices. The electronic and magnetic properties of these nanomagnets can be engineered depending on the type and decoration of adsorbed TM atom as well as the size and symmetry of the tube. Our study is performed by using first-principles pseudopotential plane wave method within spin-polarized density functional method.

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Study on electron transport properties of nanostructures

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In the last decade, many experiments and theoretical studies have been performed for the acetylene-adsorbed Si(001) surface (C_2H_2/Si(001)) since it is the initial step for the formation of silicon carbide which is expected to be applied to high-power and high-temperature electronic devices. Recently, the structure of the C_2H_2/Si(001) was experimentally investigated by using the scanning tunneling microscope (STM). Some of these studies reported that observed STM images show atomic configurations different from the actual ones, i.e., the position of C_2H_2 molecules adsorbed upon the Si dimer seems to be lower than that of the bare Si dimer.

In this study, we perform the first-principles electron-transport calculation for the tunneling current flowing between C_2H_2/Si(001) and STM tip. As the results, we obtained the calculated STM images in good agreement with experiments. The details of this work will be presented at the workshop.

Copper at the Si(001) Surface

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Cu is the preferred material for interconnects in device production but also poses a great risk to devices: Cu is highly mobile in Si even at room temperature and it can cause various device failures [1]. Theoretical studies of the interactions of Cu with the Si lattice and its defects are of key importance to understand and ultimately control the behavior of Cu in Si, limiting its detrimental effects. The surface of the Si sample is of particular interest as it appears to be a stable sink for diffusing Cu [2].

We have examined the behavior of an isolated interstitial Cu atom (Cu_i) near the Si(001) surface using density functional theory (VASP) and supercell geometries. Comparison has been made with results obtained for Cu_i in bulk Si [3]. We conclude that Cu is *attracted* to the surface region due to asymmetries in the surrounding lattice induced by surface reconstruction strain. Cu is *trapped* at the Si(001) surface due to the formation of bonds with Si surface dimer atoms. We have calculated STM images for the Cu/Si (001) local minimum energy configurations for comparison with recent experimental observations [4].

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First principles calculations of magnons in complex systems

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In itinerant magnets, spin-wave excitations can be assessed within the framework of density functionnal theory assuming adiabatic (slow) spin dynamics and applying appropriate constraints on the directions of the magnetic moments. A general approach (which avoids the use of a phenomenological Heisenberg model) was proposed to assess spin-wave dynamics [1, 2] and the dispersion relation is then given by :

$$\hbar\omega = \frac{\Delta E}{\Delta S_z}.$$

where ΔE is the change in the system energy due to a change of ΔS_z in its magnetization with respect to the ground state. A few spin-wave spectrum were already obtained using this formula for simple systems, as Fe [3, 4, 5]. Indeed, one requirement for applying the above formula is to know the exact spin-wave eigenstate. This is fixed by symmetry if there is only one atom per (magnetic) unit cell but in the case of many atoms per unit cell, the shape of the spin-wave is a priori unknown.

In our work we consider magnetic systems with many atoms per magnetic unit cell. An antiferromagnetic structure is one of the simplest such systems. The lowest branch of spin-wave excitations is given, following the above formula, by the lowest energy state with a reduced magnetic moment of ΔS_z (with respect to the ground state). We have thus included in our calculations a global constraint to tune the total magnetization. Apart from this *global* constraint, the magnetic moments are free to relax in the magnetic unit cell. The (quasi) self-consistent magnetic structure obtained then yields the structure of the spin-wave inside the unit cell.

Results will be presented for antiferromagnetic structures and compared to the usual approach using an effective Heisenberg model.

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Photophysics of $[Ru(phen)_2(dppz)]^{2+}$ intercalated into DNA: a TDDFT study

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The unique photophysical properties of the DNA-intercalating $[Ru(phen)_2dppz]^{2+}$ complex, have attracted considerable interest over the last 15 years, due to the so called "light-switch" effect. This complex does not luminesce in water but the emission is switched on by interaction with DNA. Moreover, the absorption spectrum shows Metal to Ligand Charge Transfer (MLCT) bands which are perturbed upon binding to DNA. This Ru(II) complex represents therefore a sensitive spectroscopic probe for DNA. We report the results of a combined Car-Parrinello and TDDFT investigation performed on $[Ru(phen)_2dppz]^{2+}$ isolated [1] and intercalated into an Adenine-Thymine tetramer.[2] We analyzed the electronic structure and characterized the excited states involved in the absorption and emission processes. Our results reveal a remarkable influence of the base-pairs on the nature of the excited states, which translates into a dependence of the emission spectra on the base pairs.

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Conductance, surface traps and passivation in doped silicon nanowires

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Abstract

By means of *ab initio* simulations, we investigate the structural, electronic and transport properties of p- and n-type doped silicon nanowires. We find that impurities always segregate at the surface of unpassivated wires, reducing dramatically the conductance of the surface states. Upon passivation, we show that for wires as large as a few nanometers in diameter, a large proportion of dopants will be trapped and electrically neutralized at surface dangling bond defects, significantly reducing the density of carriers. Important differences between *p*- and *n*-type doping are observed[1]. Impurities located in the core of the wire induce a strong resonant backscattering at the impurity bound state energies. Upon trapping at such surface sites, impurities become electronically inactive, yielding neither a free carrier nor inducing a significant drop of conductance. This effect is also observed for isolated surface dangling bond defects.

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Exploring water molecule and dimer by Quantum Monte Carlo

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(Dated: December 12, 2006)

Electron correlation plays a crucial role in a variety of molecular systems, ranging from hydrogen bond complexes to transition metal compounds. The commonly used approximations developed in Density Functional Theory, are nowadays not enough accurate to correctly describe the electronic structure of these systems.

Post-Hartree-Fock methods such as Configuration Interaction (CI) and Coupled Cluster (CC) have been successfully used to this purpose on a wide range of relatively small molecules. However, the bad scaling with the systems size makes these methods computationally expensive.

The good asymptotic scaling and the high accuracy of Quantum Monte Carlo (QMC) methods make them good candidates to compute the electronic structure of large and electronically correlated systems. In particular, the combination of new optimization QMC schemes with the use of a Jastrow-geminal wave function [1], has been successfully applied to study small biochemical compounds.

In the present work we apply the QMC methodology to study the binding energy of the water dimer. Total and binding energies are reported using several variational wave functions, differing on basis sets and Jastrow factor. A complete optimization of all wave function parameters (including those entering in the basis set) have been employed with the aim to build up an extremely compact representation able to fully catch the correlation effects of the system. Results are compared with CC calculation [2] and other QMC data [3]. Starting from this new approach, we will extend the study to higher complex hidrogen bonded systems such as the water phase diagram.

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First principles study of oligoacenes on Copper(100)

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Conjugated molecules and oligomers have attracted large attention in the last years due to their interesting electronic and transport properties. The interaction of these molecules with metallic surfaces is attractive both for the properties of the metal-organic interface and for the possibility of tuning the crystal structure of the films using the surface as a template. While a number of studies already exist, some basic open problems on the nature and the features of such interactions are still elusive.

In the present work we focus on a computational investigation of the class of acene oligomers (e.g. pentacene) adsorbed on Copper surfaces. We address structural and electronic properties, and we relate our results to experimental data.

We adopt an ab initio theoretical approach based on density functional theory implemented using plane-waves and ultrasoft pseudopotentials. For benzene, anthracene and pentacene on Cu(100), theoretical findings show a flat adsorption geometry with a preferential site (hollow) and a strong rehybridization of the molecular electron states in the range within 5.0 eV below the Fermi energy. The (molecular) projected DOS reveal the formation of hybrid interface states. These results lead to an interpretation of the adsorption mechanism in terms of an interaction intermediate between the physi- and the chemi-sorption regimes.

The present findings have been directly compared with experimental results from STM and angle resolved photoemission spectroscopy.

A DFT study of the interaction of Ozone with Si(001)

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The Si/SiO2 interface with its crucial application in microelectronics, is arguably the world's most economically and technically important materials interface [1]. In reaching oxide thickness in the nanometer limit, however, common manufacturing methods show their limitations, and well-accepted models of oxide growth break down. Kazor et al. [2] were the first to realize that using O3 instead of O2 as the oxidant gas allows growth at a much lower temperature (below 500°C). Subsequent experiments confirmed that ozone-grown oxides have a high film density with a low interface defect density and a much thinner structural transition layer near the Si/SiO2 interface [3]. In order to fully understand this growth process we study the initial oxidation stage through density functional theory. We will present the energetics and reaction dynamics of ozone on the Si(001) surface and suggest a microscopic oxidation model in agreement with available experimental data [4,5].

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Semiempirical, ab initio and DFT study of the complexation between α-Cyclodextrin with 4-Methyl-Pyridine

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Abstract.

Semi-empirical, *ab initio* and DFT calculations were performed on the inclusion complexation of α-cyclodextrin with 4-methyl-pyridine from a complete and unrestricted geometry optimization and conformational analysis. The complexation orientation in which the methyl group is located near the secondary hydroxyl rim of the cyclodextrin cavity (anti-parallel) was found to be preferable.

Separating electronic and ionic contributions to 3D collective surface diffusion

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Recent ^{3}He spin-echo measurements [1] on Na adatoms on Cu(001) surfaces have probed a motion of atoms also perpendicular to the surface, confined to a few tenths of an angstrom in the orthogonal direction. That motion is present when the coverage is larger than a given threshold, and is related to the translational hopping process. It could be interpreted as the adatoms changing their distance from the surface when the local concentration varies.

This atomistic interpretation is excluded by our *ab initio* simulations based on density-functional theory, and performed in the periodic multi-slab approach [2]. We simulated changes in the local concentration by the use of supercells containing more than one adatom, and by varying the relative positions. Upon optimization of atomic structures, no significant variation in the perpendicular coordinate of Na nuclei was observed for the different structures.

Instead, we suggest that the vertical motion can be interpreted purely as an electronic effect. Our findings are that the electron density, from which He atoms are scattered, is more protruded towards vacuum when the local concentration is large—following a local lowering of the electrostatic potential generated by the adatom dipoles. An effective-medium estimate of the classical turning point for the He atom reproduces the observed magnitude of the vertical motion.

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Phonons of oxidized Si clusters from first principle methods

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We have studied the influence of oxygen and oxygen-related bonds on the vibrational spectra of hydrogenated silicon nanocrystals using *ab initio* methods based on the density-functional and density-functional perturbation theory as implemented in ABINIT [1]. We have considered the non oxidized systems SiH_4 and $Si_{10}H_{16}$, and their oxidized counterparts, replacing two hydrogen atoms by one oxygen atom at various sites. The small clusters SiH_4 and H_2SiO have been used for convergence tests and their bondlegths and frequencies have been compared with experimental and theoretical reference data. The calculated density of states of the big nanocrystals show significant peaks related to the oxygen motion, which depend also on the oxygen site. Furthermore, the phonon modes have been analyzed with respect to the kind of motion, their localization in the nanocrystal, and their symmetry.

[1] `http://www.abinit.org`

Electronic excitations in Vanadium Oxide (VO_2)

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Vanadium Oxide has a metal-insulator transition at T_C = 340 K. The role of correlation in this first-order transition has been debated for a long time (see, for instance, Ref. [1,2]): is VO_2 a Peierls or a Mott-Hubbard insulator?

Despite a good agreement with experimental lattice parameters, DFT-LDA yields a negative gap in the insulating phase and hence is not able to give a good answer to this question. This seeming failure of LDA is discussed and different possible approaches to solve this problem are reviewed: from standard perturbative G_0W_0 to self-consistent GW [3,4,5]. Also results concerning other kinds of electronic excitations (in particular: electron energy loss spectra) are presented.

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Why is silver a good catalyst for Ethylene epoxidation ?

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We present a first-principles study of Ethylene Oxide (EO) synthesis on different transition and noble metal surfaces. EO synthesis is one of the most important selective oxidation processes based on heterogeneous metallic catalysis. Silver displays unique catalytic properties in the ethylene epoxidation reaction with a selectivity at high temperature and high pressure conditions up to 80% in presence of promoters such as Cs and Cl. The main undesired product is CO_2 as a result of total combustion. Even if this process is 60 years old, the detailed mechanism of the reaction is still unknown. Recently, Linic et al. have shown that on silver ethylene oxametallacycle (OMC) is a common intermediate for EO as well for acetaldehyde (Ac) formation, the latter leading to undesired total combustion [1].

Our results provide a rationale of these findings which stem from the mild reactivity of silver that hinders H–C and C–C bond breaking both in ethylene and in the OMC intermediate. By analyzing the transition state geometries toward EO and Ac we identify an indicator that strongly correlates with selectivity for EO formation and could be an useful tool in the rational search for an improved catalyst.

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***Ab-initio* calculation of the electronic *g*-tensor using periodic boundary conditions: defects in semiconductors**

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Magnetic resonance comprises some of the most powerful analytic tools in materials science. The wealth of important information available from spectroscopy, however, cannot be extracted from the experimental data alone. Experiments provide only a set of parameters which have to be compared with theoretical predictions of these quantities. Only if theoretical modelling can exclude all but one structural model, then an unambiguous identification has been achieved. In many cases the components of the electronic *g*-tensor are the only essential quantities available from magnetic resonance. In contrast to the *ab-initio* calculation of hf splittings that already do have an appreciable history, reasonable predictions of *g*-tensors making use of the machinery of *ab-initio* quantum chemistry and density functional theory (DFT) have become possible only very recently. Here, our gauge including projector augmented plane wave (GI-PAW) approach allows an *ab-initio* calculation of the all-electron magnetic response including the electronic *g*-tensor if using periodic boundary conditions.

After presenting an evaluation of the method taking nitrogen defect complexes in diamond as an example, we report on first successful applications of our method on defect identification in semiconductors: besides an unambiguous identification of the nitrogen-vacancy pair N_CV_{Si} in 6H-SiC, neutral nitrogen donor pairs on inequivalent carbon lattice sites are proposed as an defect model for the so-called N_x-lines in 4H-SiC contributing to a saturation of the free-carrier concen-tration observed in heavily nitrogen doped SiC.

Half-metallicity at $Co_2Cr_{0.5}Fe_{0.5}Al/GaAs(001)$ heterostructures

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The stability, electronic and magnetic properties of $Co_2Cr_{0.5}Fe_{0.5}Al$ interfaces on GaAs substrate along the [001] direction were studied within the framework of density functional theory by using the plane wave pseudopotential approach (PWscf). The phase diagram obtained by the ab initio atomistic thermodynamics shows that in practice the CrAl/As termination is stabilized under suitable conditions.We additionally investigated the half-metallicity of all ideal interfaces along the same direction and found out that the CrAl/As termination has the highest spin polarization. Furthermore, the spin resolved band-alignment for CrAl/As interface were extracted as a technologically relevant quantity for the electronic and spintronic properties of layered devices.

Conformations vs. Interaction energy: adsorption of complex molecules onto metallic surfaces, the case of amino acids

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By means of extensive finite electronic temperature density functional calculations, we study the adsorption of benzene, alanine and phenylalanine onto Pt(111), Ni(111), and Ag(111) metallic surfaces. Since phenylalanine can be thought as a highly flexible composition of alanine and benzene, we investigate the interplay between the statistically accessible conformations (in vacuo or near a surface) and the energetics of the adsorption. In particular, we find that the most energetically favored configurations are the least likely to be sampled by the molecule near the surface. We complete the study by analyzing the different contributions to the interaction energy (viz. chemical and electrostatic).

Structural and vibrational properties of Silicon nanotubes

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There is currently a strong interest for the integration of nanomaterials into the present Silicon device technology. The production of Si-based nanotubes would open interesting new possibilities. Si nanotubes have been recently observed in nanostructured Si samples obtained by different techniques [1-3]. The morphology of the observed quasi-one-dimensional structures is not yet well established, but some samples have been claimed to contain single-wall nanotubes (SWNT), others multi-walled nanotubes.

Raman spectroscopy is especially well-suited and has been extensively used for the characterization of Carbon nanotubes. For this reason we have calculated the vibrational properties of selected models for Si SWNT, using first-principle DFT techniques. Unlike C nanotubes, Si nanotubes have a "puckered" structure, i.e. Si atoms are displaced alternatively inwards and outwards at the tube surface. This distorsion, already visible in the Si equivalent of a graphene sheet, reflects the preference of Si for a sp^3 configuration over the planar sp^2 configuration. Our results indicate that the most intense Raman mode is a tangential mode with slightly higher frequency ($\sim$ 550 cm^{-1}) than the optical mode in crystalline Si. The most intense IR mode has a very similar frequency to that of the Raman mode.

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Unconstrained Variational Determination of the Kohn-Sham Potential

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Abstract

I present a method that highlights the physical meaning of the Kohn-Sham (KS) scheme in Density Functional Theory (DFT) and provides a bridge between DFT and traditional wave function methods. In this theory, the KS potential emerges as the optimal effective potential in an unconstrained minimization that does not involve fixing the ground state single-particle density. The method leads to ab initio expressions for the correlation energy functional that are based on second or higher order many-body perturbation theory. The second order expression is variational and consequently cures the unphysical behaviour seen by other recent ab initio approaches to the correlation energy and potential in DFT.

N.I. Gidopoulos, arXiv:cond-mat/0603277, 2006

Molecular quantum chemistry methods applied to the solid state: cohesive energy of ionic materials

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Density functional theory (DFT) has provided the foundation for the quantum-based modelling of condensed matter over the past 20 years. Nevertheless, it is widely recognised that DFT often falls far short of chemical accuracy (1 kcal/mol, 0.05 eV/atom, or 2 mE_h/atom) for many types of problem, particularly in surface science, but attempts to develop systematic improvements have met with mixed success. Quantum chemistry techniques, by contrast, place a strong emphasis on systematic improvement of the description of electron correlation. A number of schemes have been proposed [1] for using high-level quantum chemistry to calculate the energetics of condensed matter, but none of them has yet been widely adopted. We present here a simple strategy for calculating the cohesive energy of certain kinds of crystal using readily available quantum chemistry techniques [2]. The strategy involves the calculation of the electron correlation energy of a hierarchy of clusters, and the cohesive energy E_{coh} is extracted from the constant of proportionality between these correlation energies and the number of atoms, in the limit of large clusters. We apply the strategy to the LiH crystal, using the MP2 and CCSD(T) schemes for the correlation energy, and show that for this material, E_{coh} can be obtained to an accuracy of ~30 meV per ion pair, this accuracy being confirmed by comparison with the experimental value, after correction for zero-point energy and temperature effects. Preliminary work on the extension of this method to the cohesive energy of other materials, including LiF and MgO, as well as the adsorption energy of molecules on surfaces, will be presented.

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CURRENT INDUCED FORCES ON ADATOMS ON CARBON NANOTUBES

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We have investigated the current-induced forces acting on atoms (B, C, N, O, and F) adsorbed on metallic carbon nanotubes (CNT) by using the density-functional theory (DFT) together with the nonequilibrium Green's function (NEGF) technique. In the case of a (5,5) metallic nanotube we observed forces pushing the negatively charged atoms[1] (N, O, F) in the direction of the electron flow and positively charged atoms (B, C) in the opposite direction. Remarkably larger forces, perpendicular to the CNT layer, were found to be independent of the current direction: they push C, N, O and F away from the tube's surface but pull B closer to it. The unexpected features of current-induced forces obtained in the present study seem to come from a combined nature of electrostatic and momentum-transfer interactions between adatoms and electric current[2]. We discuss the detailed properties of forces on many kinds of adatoms at various adsorption sites.

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First-principles study of the lattice dynamics of multiferroic $BiFeO_3$

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Bismuth ferrite ($BiFeO_3$) constitutes a prototypical multiferroic compound that, in its R3C ground-state structure, combines both ferroelectric and almost anti-ferromagnetic orders. Although, $BiFeO_3$ has been widely studied during the recent years, many questions concerning the proper interpretation of its experimental phonon spectra remain. Here, we report the first density functional theory (DFT/LDA) calculation of both the infrared (IR) and Raman spectra of $BiFeO_3$, and propose an assignment of the main experimental lines. This constitutes a reference calculation useful to help understanding the evolution of the phonon frequencies around the magnetic and ferroelectric phase transition temperatures and to try clarifying the mechanism of these phase transitions.

Pseudopotential GW calculations for wurtzite ZnO

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ZnO is a wide band gap II^B-VI semiconductor with interesting applications for optoelectronics, spintronics, piezoelectric devices and chemical sensors. Like the other II^B-VI compounds, its properties are largely influenced by the interaction and hybridization of semicore cation *d* electrons with anion *p* valence electrons. In a pseudopotential based ab-initio study of the electronic properties of ZnO is thus essential to treat semicore *d* states as valence states. It is know, however, that DFT, besides underestimating the band gap, as is usual for semiconductors, predicts also an underbinding of semicore *d* states which result located too high in energy. This has the consequence of enhancing the *p-d* coupling, pushing up the valence band maximum and further reducing the band gap. The subsequent application of GW self-energy corrections can be therefore not so effective in reproducing experimental data.
In this work we compare GW band structure calculations for wurtzite ZnO based on DFT ground states obtained with three different pseudopotentials for Zn: Zn^{2+}, Zn^{12+} and Zn^{20+}. The first one corresponds to freeze semicore *d* electrons into the core. Even if the use of this pseudopotential is known to provide inaccurate results, it is instructive to employ it to show the effect of reducing to zero the cited *p-d* coupling. The second pseudopotential, Zn^{12+}, contains both 3*d* and 4*s* states, whereas Zn^{20+} includes also 3*s* and 3*p* states in the valence. It is shown how considering the whole Zn third shell in the pseudopotential result crucial for a proper description of ZnO band structure. Preliminary results for the optical properties of ZnO are also presented.

Accuracy and error bars of DFT calculated thermodynamic properties for elementary metals

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A continuously growing demand to provide ab initio calculated input for higher-level simulations is noticeable in various fields of activity. The aim is an efficient and tailored design of materials. The scope of such ab initio calculations extends well beyond ground state calculations heading towards the description of materials at their operating temperatures. At finite temperatures, the main challenges are entropy contributions arising e.g. from lattice vibrations, possible configurations, and magnons.

We have performed a systematic study to check the reliability and accuracy of common xc-functionals (LDA, GGA-PBE) in predicting thermodynamic properties arising from lattice vibrations. We have therefore calculated phonon dispersions, Grüneisen parameters, free energies, thermal expansions, and heat capacities for a large set of fcc-metals (Cu, Ag, Au, Pd, Pt, Rh, Ir, Pb, and Al). The calculations have been performed employing a plane-wave PAW approach (VASP) and within the quasiharmonic approximation. In order to clearly assign the error bars to the employed functional, careful convergence checks with respect to cell size (up to 256 atoms), k-point sampling (up to 55000 k-points per atom), and real space mesh used to calculate the augmentation charges have been performed. Our results show that integral quantities such as the Grüneisen parameter or the free energy rapidly converge, while an accurate determination of phonon energies requires large unit cells and k-point sets. A comparison with available experiments reveals an excellent agreement with the experimental data lying in-between the LDA and GGA results. The computed free energies systematically agree with the experimental data (as provided by the CALPHAD method) up to a temperature of 950K to within a range of 1kcal/mol.

Keywords: PAW-method, metals, thermodynamic properties, CALPHAD

Understanding the macroscopic limit of time-dependent density-functional theory

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Time-dependent density functional theory is a rather accurate and efficient way to compute electronic excitations for finite systems (clusters and molecules). However, in the macroscopic limit (systems of increasing size), for the usual adiabatic random-phase and local-density approximations, one recovers the incorrect Kohn-Sham independent-particle picture, where the excitonic effects are misdescribed, and the band gap is incorrect.

To clarify this trend, we investigate the large-N limit (N number of atoms) of several forms of the time-dependent kernel by means of numerical and analytical analysis of tight-binding models of 1-D and 3-D systems.

Density Functional Calculations of Adsorption of Palladium on CNT Surface

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Abstract:The adsorption of single, double and triple Pd layers on metallic carbon nanotubes (CNT) has been investigated by first principles all electron quantum calculations within the density functional theory. The binding energies and geometries of stable adsorbed layers have been calculated. We have found a new type of adsorbed Pd layer if compared with those adsorbed on graphene. Owing to the curvature effect of a carbon nanotube the adsorbed layers are strongly bounded with CNT. Our results indicate that due to a large surface to volume ratio a CNT covered with a thin Pd layer may work as a catalyst more effectively than traditional materials. We expect that CNTs with Pd layer show potential interesting applications as a hydrogen sensors or rapidly acting hydrogen storage materials.

Absorption spectra in solution : combining Quantum Monte Carlo with QM/MM Car-Parrinello Dynamics

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Accurate calculations of molecular excitations in solution and in condensed complex environments like proteins are still a challenge for both Density Functional Theory and other quantum chemistry methods. Recently, it has been shown that Quantum Monte Carlo (QMC) can accurately estimate excitation energies even in delicate cases like conjugated systems [1]. In the present contribution we extend the use of QMC to mixed quantum - classical models to allow a many-body study of electronic excitations for biological chromophores in situ. Using a Jastrow-Slater trial wave function we calculate the QMC absorption spectra of small molecules in solution using snapshots of Car-Parrinello QM/MM trajectories [2,3]. The effect on the excitation energy of the solvent environment, of the basis set, and of the trial wave function will be also discussed.

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A study of reversible phase transition by pressure in calcined and containing Xe zeolite A *via* energy minimization calculations

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Abstract

In order to study the reversible phase transition of the zeolite A under external high pressure, energy minimization calculations in this material have been performed. This problem has been in the focus of the researchers recently [Y. Huang, E.A. Havenga, *Chem. Phys. Letter*, 245, 65 (2001), J. Gulín-González, G.B. Suffritti, *Microp. Mesopor. Materials*, 69, 127 (2004), I. Peral, J. Iñiguez, *Phys. Rev. Letter*, 97, 225502 (2006)]. The simulations show that the exchangeable cations (Na^+ and Li^+) play an essential role in the amorphization process. To consider the potential effect of the molecular species on the reversibility process, energy minimizations were performed for containing Xe zeolite A. Overall, the results suggest that the reversibility of the phase transition is independent on the presence of guest molecular species. Finally, the simulations show the importance of the structural topology (particularly, the D4R secondary units) in the recovering of the crystalline order. The results reported in this paper could facilitate to understand the mechanism of structural memory in nanoporous materials.

Study on the maximum accuracy of the pseudopotential-density functional method with localized orbitals *vs.* plane waves basis sets

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A detailed study on the accuracy attainable with localized numerical orbitals in the context of pseudopotential first-principles density funcional theory is presented. Dimers of first- and second-row elements are analyzed: bond lengths, atomisation energies and Kohn-Sham eigenvalue spectra obtained with localized orbitals and with plane waves basis set are compared. Numerical orbitals are optimized following two different strategies: a) variational optimization of the localized orbitals by maximizing the projection (onto such basis) of the wavefunctions obtained in plane waves calculations (i.e. minimization of the charge spillage); b) minimization of the total energy of the dimers with respect to a set of primitive orbitals (in this case the OpenMX software was used). For each dimer the cutoff radius, the shape and the number of atomic basis orbitals are varied in order to maximize the accuracy of the calculations. It is found that even a small set of optimized localized orbitals is enough to attain a very good accuracy.

Tight-binding molecular dynamics study of photo-induced volume changes in amorphous Selenium

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We have investigated the microscopic processes in chalcogenide glasses which are caused by light illumination. We applied tight-binding molecular dynamics simulation to follow the atomic dynamics. After photon absorption we treated the excited electron and hole independently. We found covalent bond breaking in amorphous networks with photo-induced excited electrons, whereas excited holes contribute to the formation of inter-chain bonds. We also observed a correlated macroscopic volume change of the amorphous sample. The interplay between photo-induced bond breaking and inter-chain bond formation leads to either volume expansion or shrinkage. Our results provide a new and universal description, which can explain simultaneously the photo-induced volume expansion and shrinkage. In the non-ideal case, a part of the microscopic processes is irreversible and the total expansion includes the reversible and irreversible changes. Our explanation can handle this macroscopic effect, too. The model is supported by the results of recent measurements carried out by Y. Ikeda and K. Shimakawa.

The discontinuity of the chemical potential in reduced-density-matrix functional theory

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Reduced-density-matrix-functional theory (RDMFT) [1] is one possible way to treat electron correlation beyond density-functional theory. In order to calculate the fundamental gap we generalize RDMFT to fractional particle numbers. For each fixed particle number, M, the total energy is minimized with respect to the natural orbitals and their occupation numbers. This leads to a function, E^M_{tot}, whose derivative with respect to the particle number has a discontinuity identical to the gap. The formula for the calculation of the fundamental gap is derived and its application to open-shell systems is discussed.

Numerical results are presented for alkali atoms and small molecules and the performance of different functionals [2] as well as the changes due to different basis sets are discussed. Also, we investigate the importance of varying the natural orbitals for the calculation of the fundamental gap.

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An evolution-operator method for density functional calculations

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We present the implementation of a fast real-space algorithm for density functional calculations of atomic nanoclusters. A prerequisite for electronic structure calculations of realistic systems is a fast and reliable method to solve the Kohn-Sham eigenvalue problem for non-local potentials of the Kleinman-Bylander type. The method we present here uses a fourth-order factorization of the evolution operator $e^{-\epsilon H}$, and improves the computational efficiency by about an order of magnitude compared to conventional second-order schemes. The efficiency and accuracy of the method is demonstrated for the examples C_6H_6 and C_{60}.

OsN_2: crystal structure and electronic properties

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Osmium nitride belongs to a family of nitrides synthesized recently at high pressures from their parent elements. Here we show, based on first-principles calculations, that the crystal structure of osmium nitride is isostructural to marcasite. Excellent agreement is obtained between our results and x-ray, Raman and compressibility measurements. In the OsN_2 marcasite structure single-bonded N_2 units occupy the interstitial sites of the Os close-packed lattice, giving rise to a metallic compound. A comparison between the formation energies of OsN_2 and PtN_2 explains the similar thermodynamic conditions of formation reported experimentally for the two compounds.

Determination of symmetry reduced structures by a soft-phonon analysis in magnetic shape memory alloys

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Ni_2MnGa is a typical example of a Heusler alloy that undergoes a martensitic transformation. In the high-temperature austenitic phase it has a cubic $L2_1$ structure, whereas below 200 K the symmetry is reduced by an orthorhombic distortion. Despite lattice deformations of more than 6% and large strains connected to this change, it is completely reversible. Therefore, Ni_2MnGa serves as a shape memory compound. The fact that Ni_2MnGa additionally orders ferromagnetically below 360 K makes the material particularly attractive for applications as actuators and sensors. Nevertheless, its structural details in the martensitic phase are still a subject of much debate. Several shuffling structures have been observed experimentally. The temperature dependent transformations between these structures need to be understood for an improvement (operation with e.g. higher reliability and smaller magnetic fields) of the magnetic switching.

In order to identify the stable structures and the low energy transition paths, we calculated free energy surfaces as function of key reaction coordinates (lattice constants, c/a-ratio) in DFT. (The GGA xc-functional and the PAW approach were used in these investigations.) The different variants of the low symmetry orthorhombic structures lead to characteristic minima at this surface. However, the ab initio determination of the experimentally observed shuffling structures is challenging, due to the large phase space of possible atomic positions and the small shuffling formation energies of only a few meV per unit cell. Hence, we used the quasiharmonic approximation in order to compute and analyze phonon spectra. Starting with the symmetric structure of the austenite, the TA_2 phonon dispersion showed a phonon softening along the [110] direction. We were able to extract detailed information about the kind of this lattice instability from the eigenvectors of the unstable phonon modes. By setting up the corresponding modulated harmonics in supercell calculations, we systematically and efficiently identified stable shuffling structures. The resulting structural phases (austenite, martensite, pre-martensite) were compared with recent experiments.

Keywords: shape memory, free energy, martensitic phase transition, phonon softening

Amorphization induced by pressure: results for zeolites and general implications

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We report an *ab initio* study of pressure-induced amorphization (PIA) in zeolites, which are model systems for this phenomenon. We confirm the occurrence of low-density amorphous phases like the one reported by Greaves *et al.* [Science **308**, 1299 (2005)], which preserves the crystalline topology and might constitute a "perfect" glass with very small configuration entropy. The role of the zeolite composition regarding PIA is explained. Our results support the correctness of existing models for the basic PIA mechanim, but suggest that energetic, rather than kinetic, factors determine the irreversibility of the transition.

For more information, visit http://www.icmab.es/dmmis/leem/jorge

Optical Spectra of doped Silicon Nanocrystals

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Abstract

The absorption and the emission spectra of doped silicon nanocrystals including geometry optimization have been calculated within a first-principles framework. Starting from hydrogenated silicon nanocrystals, simultaneous *n*- and *p*-type doping with boron and phosphorous impurities have been considered. We found that the B-P co-doping results easier than simple B- or P-doping and that the two impurities tend to occupy nearest neighbours sites rather than other positions inside the nanorystal itself. The co-doped nanocrystals present band edge states localized on the impurities that are responsible of the red shifted absorption threshold with respect to that of pure un-doped nanocrystals in fair agreement with the experimental outcomes. The emission spectra show then a Stokes shift with respect to the absorption due to the structural relaxation after the creation of the electron-hole pair. Moreover the absorption and emission spectra have been calculated for a small co-doped nanocrystal by going beyond the single particle approach through the self-energy correction and the Bethe-Salpeter equation scheme showing the important role played by the many-body effects.

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THE INTERACTION OF GOLD SURFACES WITH BIOMOLECULES: TOWARDS A MULTISCALE APPROACH

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To describe properly the interactions between a gold surface and biomolecules in a classical Molecular Dynamic simulation, it is necessary to generate models accounting for induced polarization effects inside the metal (i.e. the image charge effect).

The introduction of charged “fictitious” atoms, bonded with each gold atom, is a simple but effective manner of incorporating such polarization effects, with a still manageable computational effort.

Systematic parameterization of the required variables such as mass and charge values for the imaginary atom or the force constants of its bond with the gold atom, is presented.

Preliminary results support our method as a reduction of the error introduced when neglecting metal polarization effects is obtained.

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First Principle modelling of Infrared spectrum of Cyclohexene-2-Ethanamine

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We have performed structure of cyclohexene-2-ethanamine with the first principle method and experimental IR data. Vibrational properties of this molecule is reported for with assignments for related molecules in the range of 4000-400cm^{-1}. The theoretical method of these calculations is based on plane-wave pseudopotentials calculations in local density approximation (LDA) and generalized gradient method (GGA). Equilibrium geometric structures are obtained by pseudo potentials. A remarkable agrement was obtained between theory and experiment, especially on position of the stretching bands of NH groups.

Keywords: First Principle, Pseudo potentials, Plane-wave, Cyclohexene-2-ethanamine.

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An evolution-operator method for density functional calculations

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We present the implementation of a fast real-space algorithm for density functional calculations of atomic nanoclusters. A prerequisite for electronic structure calculations of realistic systems is a fast and reliable method to solve the Kohn-Sham eigenvalue problem for non-local potentials of the Kleinman-Bylander type. The method we present here uses a fourth-order factorization of the evolution operator $e^{-\epsilon H}$, and improves the computational efficiency by about an order of magnitude compared to conventional second-order schemes. The efficiency and accuracy of the method is demonstrated for the examples C_6H_6 and C_{60}.

First Principles Calculation of p-type scattering in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$

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First principles density functional theory is used to calculate the mobility of holes in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys as a function of alloy composition. The alloy host is modelled within the virtual crystal approximation (VCA) using supercell techniques. The scattering matrix for carrier scattering in the presence of a Ge or Si substitutional atom in the VCA lattice is determined from the resultant energy splitting in the valence bands. The effect of the spin-orbit interaction is included in these calculations. The mobility is obtained from the scattering rate using the Boltzmann transport equation in the relaxation time approximation.

Nanoscale Smoothing and the Analysis of Interfacial Charge and Dipolar Densities

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The interface properties of interest in multilayers include interfacial charge densities, dipole densities, band offsets, and screening-lengths, among others. Most such properties are inaccesible to direct measurements, but are key to understanding the physics of the multilayers. They are contained within first-principles electronic structure computations but are buried within the vast amount of quantitative information those computations generate. Thus far, they have been extracted from the numerical data by heuristic nanosmoothing procedures[1–3] which do not necessarily provide results independent of the smoothing process. Here we develop the theory of nanosmoothing, establishing procedures for both unpolarized and polarized systems which yield interfacial charge and dipole densities and band offsets invariant to the details of the smoothing procedures when some especific criteria are met. We discuss in detail these criteria. We show also that dipolar charge densities, i. e. the densities of charge transferred across the interface, and screening lengths are not invariant. We illustrate our procedure with a toy model in which real, transversely averaged charge densities are replaced by sums of Gaussians.

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An evolution-operator method for density functional calculations

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We present the implementation of a fast real-space algorithm for density functional calculations of atomic nanoclusters. A prerequisite for electronic structure calculations of realistic systems is a fast and reliable method to solve the Kohn-Sham eigenvalue problem for non-local potentials of the Kleinman-Bylander type. The method we present here uses a fourth-order factorization of the evolution operator $e^{-\epsilon H}$, and improves the computational efficiency by about an order of magnitude compared to conventional second-order schemes. The efficiency and accuracy of the method is demonstrated for the examples C_6H_6 and C_{60}.

Ab initio study of native defect of CaB_6

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Through first-principles pseudopotential calculations, we investigated the electronic structures of CaB_6 and native defects and the formation enthalpies. In the CaB_6 crystal, strong covalent bonding between the nearest B atoms is found and the Ca atom is positively ionized. The calculational results for the spin polarizations of defects indicate that robust ferromagnetism is not available from the defects. It is proposed that the B-antisite, forming a B_7 structure, provides an explanation for the n-type conductivity of the Ca-deficient CaB_6.

Change in electronic structure and degradation of field emission from carbon nanotubes by CH_3 adsorption

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In order to find the microscopic origin of the degradation of the carbon nanotube(CNT)-based field emission display(FED), we calculate the total energy and electronic structures of the methyl(CH3)-adsorbed (5,5) CNT with or without external electric fields. Because an organic paste is used for attaching CNTs to the electrode in a CNT-based FED, organic gases and radicals could be produced from it and affect the field emission. We have found that a methyl radical is strongly bound to the CNT and the binding energy does not decrease as the number of adsorbed methyl radicals increases. A methyl radical adsorption induces the spin polarization of the CNT and changes one sp^2 carbon in CNT to a sp^3 carbon. It also changes the electronic structure considerably. A methyl radical adsorbed on the wall is a source of high resistance and removes a state localized on the tip which gives, in the pristine CNT, a dominant contribution to the emission current. We suggest that radicals such as CH_3 are critical for the degradation of the CNT during the field emission.

Quasiparticle corrections to the LDA+U electronic structure of bcc hydrogen.

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Abstract

The electronic structure of solid hydrogen in the body-centered cubic crystal structure is studied by the introduction of self-energy corrections within the *GW* approximation to the LDA+U energy eigenvalues. The *GW* method has been shown to work for a wide variety of physical systems for which the ground state is accurately described by the standard DFT methods like LDA and GGA. However, these methods fail qualitatively for systems with strongly correlated electrons. On the other hand, the localized nature of the electrons in these systems is well described by LDA+U, which introduces a Hubbard-like U term to account for the strong on-site Coulomb repulsion. We combine the two methods, LDA+U and *GW*, to study bcc solid hydrogen, a model system that exhibits correlation effects.

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Density functional study of high pressure phases in II-VI semiconductors

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The study of pressure induced phase transitions has been rapidly expanding field of research during the past few decades. It was discovered that many semiconductors have a rich phase diagram, as a function of pressure and temperature, with a number of phases, which were not known before. The understanding of the mechanism of high pressure phase transitions at microscopic level is far from complete and more theoretical models are required.

We investigated the stability of the rocksalt structure with respect to the high pressure Cmcm structure was investigated for several II-VI semiconductors (ZnS, ZnSe, CdS and CdSe). The lattice dynamics calculations reveal that the rocksalt structure is unstable with respect to transversal acoustic mode at the Brillouin zone boundary. The phase transition is of the second order, associated with cell doubling in the high pressure Cmcm phase with frozen in deformation. Since the volume change at the transition is very small or zero in all studied crystals, transitions were estimated from the pressure at which the frequency of zone boundary transversal acoustic mode goes to zero.

The observed pressures of the phase transitions in structural measurements were reproduced more accurately then in previous calculations and the difference between observed and calculated transition pressure is well below 10 %.

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Solvation structure and transport of acidic protons in room temperature ionic liquids

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A description of the energetics, solvation structure and diffusion of acidic protons in ionic liquids is important for acid-based chemistry in room temperature ionic liquids, and for the design of new proton-conducting materials. In this work we present the results of adding a molecule of HCl to dimethyl-imidazolium chloride ([mmim][Cl]). First-principles molecular dynamics simulations show that the acidic proton exists as the symmetric, linear species [$ClHCl^-$]. The solvation structure around this ion is analysed, and it is shown that, as the anion is stretched in the direction of forming the [HCl] and [Cl^-] species, the first Cl becomes less coordinated with the protons in the cations of the solution while the second one gains coordination.

The proton transport mechanism is investigated by applying a force along the asymmetric stretch coordinate until the ion breaks. This results in the exchange of one of the Cl atoms with a neighbouring chloride belonging to the solvent to form a new [$ClHCl^-$] molecule. Such a process results in an effective hopping of the hydrogen atom. The reaction mechanism is discussed in terms of the structure of the reacting species and their solvation shells. An estimation of the associated free energy change is provided. In this particular case the hopping activation barrier appears to be higher than the barrier for diffusion of the [$ClHCl^-$] species as a whole. This, however, does not discard a hopping contribution to the proton conductivity in this compound, and it also suggests that other room temperature ionic liquids can be designed, where hopping is the dominant proton conduction mechanism [1].

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Elastic and Vibrational Properties of Cobalt Under High Pressure

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Understanding the high pressure properties of metals is important for high pressure physics as well as materials properties. The studies on 3d elements attract interest due to their uncommon properties such as the dramatic changes in crystal structure through d series, the wrong ground state prediction of local spin density approximation for Fe and magnetoelastic effects in Co.

Under ambient conditions, Co crystallizes in hcp geometry and is stable in that phase up to 100 GPa. In the pressure range of 105-150 GPa it undergoes a phase transition to fcc phase. Both first principles calculations and experiments on density and compressibility predict a non-magnetic fcc phase after transition but the mechanism of transition is not fully understood yet.

In this study, we investigate the energetics, elasticity and lattice vibrations of cobalt up to 400 GPa by using density functional theory. According to our results on pressure evolution of magnetization and equation of state, the ground state properties of cobalt are well reproduced, the phase transition is predicted to be first order from hcp ferromagnetic to fcc non-magnetic phase. We also report the pressure evolution of single crystal and aggregate elastic constants as well as phonon dispersion relations for a better understanding of the hypothesis of magnetoelastic coupling. Finally we discuss the correlation between magnetization and predicted abnormal elastic properties and compare our results with the experimental data.

Surfactants and Ordering in Films of III-V Alloys

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Alloying two semiconductors and varying the composition is a well known procedure of band-gap engineering. An additional mechanism for fine tuning of electronic gap E_g consists in controlling the degree of atomic ordering; as it turns out, the latter can be influenced by adding surfactants during the growth. In this work we study systematically the energetics of disordering in six ternary III-V alloys, with and without surfactants (Sb, Bi, Ga, As, P tested). We study the 50%+50% alloys (assumed in the *CuPt-B* structure and with the $\beta 2(2\times 4)$-reconstructed surfaces), and the sensitivity of the system to disordering is probed by exchanging two cations (or anions) of the cationic (or anionic) sublattice, in presence and absence of the surfactant. The question posed is whether, and how, the propensity to disordering is modified by the selected surface agent. In the case of (In,Ga)P alloy we find that the energetic cost of In $\longleftrightarrow$ Ga interchange ($\Delta E = 0.61$ eV/pair) shrinks to nearly zero upon addition of Sb or Bi on the surface. Depositing As instead will, on the contrary, leave the ΔE practically unchanged. These computer experiments corroborate with empirical findings. The same methodology is applied to (In,Ga)As, Ga(As,P), In(As,P), Ga(As,Sb), and In(As,Sb) alloys, and it is found which atoms and on which alloys act as either good or inefficient surfactants.

Ab initio molecular dynamics study of the calcite-water interaction

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Density functional theory calculations were employed to explore the interaction between water and the (10.4) surface of calcite. Previous experimental evidence has suggested dissociation of water molecules in this system. Static relaxations of both associated and dissociated water molecules revealed the latter to be energetically unfavourable, although a metastable dissociated state was found. Surface and adsorption energies were compared for water molecules placed at several positions on the crystal surface. These indicated a preference for the molecule to sit across the crystal with each hydrogen directed towards a different carbonate row. *Ab-initio* molecular dynamics simulations confirmed that this was the favoured position. Further molecular dynamics using a monolayer of water displayed a clear 'herring bone' pattern. All the water molecules in the monolayer remained associated, although elongation of the bonds indicated a tendency towards dissociation.

The non-local correlation in Density Functional Theory calculations

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An important aspect of the development of the Density Functional Theory (DFT) is the improvement of functionals beyond the currently most widely used Generalized Gradient Approximations (GGA) [1]. Tractable schemes have been proposed for including the non-local correlation into the functional [2,3]. This is a major improvement in the case of weakly interacting neutral atoms or molecules, since it includes the van der Waals attraction. Recently we have applied the 'asymptotic' approach which divides the system into weakly coupled fragments of atoms or clusters [2] to the chemisorption of Xe monolayers on Cu(111) and Pt(111) surfaces [4]. Here we also consider the 'seamless' approach which uses a new non-local correlation functional [3], and apply it to several cases, from noble gas atoms to bulk matter. It looks promising even for strongly interacting systems, but needs further improvement both in numerical evaluation procedure and in the treatment of the exchange [5].

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Infrared and Raman spectra of silica polymorphs from an ab-initio parameterized polarizable force field

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The general aim of this study is to test the reliability of polarizable model potentials for the prediction of vibrational (Infrared and Raman) spectra in highly anharmonic systems such as high temperature crystalline phases. By using an ab-initio parameterized interatomic potential for SiO_2 and molecular dynamic simulations, we calculate the infrared and Raman spectra for quartz, cristobalite and stishovite at various thermodynamic conditions. The model is found to perform very well in the prediction of infrared spectra. Raman peak positions are also reproduced very well by the model, however, Raman intensities calculated by explicitly taking the derivative of the polarizability with respect to the atomic displacements are found to be in poorer agreement than intensities calculated using a parameterized "bond polarizability" model. Calculated spectra for the high temperature β phases, where the role of dynamical disorder and anharmonicities is predominant, are found to be in excellent agreement with experiments. For the octahedral phases, our simulations are able to reproduce changes in the Raman spectra across the rutile-to-$CaCl_2$ transition around 50 GPa, including the observed phonon softening.

A comparative study of electronic band structures of hydrogen-terminated silicon chains by density functional theory with and without GW corrections

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Abstract:

Theoretical predictions of electronic band structures of low dimensional nanostructures are important for the development of nanoscience and nanotechnology. However, the conventional density functional theory (DFT) is suspected to be unreliable for this purpose. To verify the validity of DFT, we performed comparative studies of the electronic band structures of hydrogen-terminated silicon chains with <100>, <110> and <112> orientations by DFT scheme with and without GW corrections. It is found that the both levels of theory predict the same band structure features: the former two silicon chains are direct band gap systems and the latter one manifests an indirect band gap. The GW correction to the LDA energy difference of the minimum of the conduction bands at Γ and X points is within 0.02 eV. This study is expected to lend credit to the DFT for qualitative determination of electronic band structures of low dimensional systems.

Key words: Density Functional Theory, Plane Wave, GW, Electronic Band Structure

Second order harmonic generation in crystalline semiconductors

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A comprehensive understanding of the nonlinear optical properties of solids is crucial for the improvement of nonlinear materials and devices and provides an opportunity to search for new materials. However, the theoretical description of nonlinear effects in solids is a formidable task and important difficulties have delayed any accurate calculations for many years.

We formulate a derivation for the calculation of second-order susceptibility tensor for crystals of any symmetry, [1]. For cubic symmetries, we show how this approach can be simplified and expressed in terms of the second-order response function and of the dielectric function.

Numerical results will be presented for SiC and GaAs

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Optical Properties of Bulk CaF_2 and its *F* Center

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We present the quasiparticle band structures and optical excitation spectra of bulk CaF_2 and of the *F* center in CaF_2 using first-principle methods. The quasiparticle band structures are evaluated in Hedin's GW approximation. Thereafter, the electron-hole interaction is calculated and the Bethe-Salpeter equation is solved, yielding the optical absorption spectra. Particular attention is paid to the Ca 3*d* states, which contribute to the lower conduction bands, and to the Ca 3*s* and 3*p* semicore states, which must be included in the GW method as valence states. The calculated quasiparticle band gap of bulk CaF_2 is 11.5 eV, which is in agreement with experiment (11.8 eV). The calculated optical absorption spectrum and reflectivity spectrum of bulk CaF_2, which consist of an exciton peak at 10.7 eV and several resonant-exciton peaks between 12 eV and 16 eV, are in good agreement with experiment. The first exciton peak corresponds to the excitation from the occupied F 2*p* orbitals to the *s* orbitals at the Γ-point of the lowest unoccupied conduction band.

One of the most prominent point defects of CaF_2 is given by the *F* center, i.e. a fluorine vacancy. The *F* center is characterized by a hole level which we find 6.6 eV above the top of the valence band. An exciton peak is observed at 3.5 eV for *F* center, which corresponds to the *F* center optical absorption peak (3.3 eV) observed in experiments. The excited electron is localized at the Ca atoms and F atoms surrounding the vacancy, exhibiting *d*-orbital character and *p*-orbital character, respectively. The hole occupies the *s* orbital centered at the vacancy and the *p* orbitals centered at the surrounding Ca atoms and F atoms.

First-principles study of the electronic structure of cubic GaS: metallic versus insulating polymorphs

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The electronic structure of different polymorphs of gallium sulphide (GaS) with cubic structure is investigated by means of first-principles band structure calculations in connection with experimental reports on a metastable semiconducting cubic form of this material [1, 2]. The expected metallic character of simple cubic phases containing one GaS group per unit cell (rocksalt or zincblende) is confirmed by the calculations. A cubane based zincblende structure is found to exhibit a band gap which is compatible with experimental results but the unit cell parameter is much larger than the reported ones. We have also studied cubic phases containing hydrogen. It is found that two insulating polymorphs can be stable: i) a simple cubic structure based on $[HGaS]_4$ cubane units and, ii) an insulating zincblende structure in which hydrogen atoms occupy the empty sites of the cubic unit cell. The last structure seems to be the more likely structural alternative for the phase so far described as a semiconducting cubic phase of GaS. The presence of hydrogen could explain the reported instability of cubic GaS under thermal annealing.

Physical Review B, *in press*

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Self-consistent solution of the optimized effective potential equations for metal clusters in jellium model

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Abstract

In this work, using the exchange-only orbital dependent functional, we have obtained the optimized effective potential using a simple iterative method [1]. Using this method, we have solved the self-consistent Kohn-Sham equations for closed-shell simple metal clusters of Aluminum, Lithium, Sodium, Potassium, and Cesium in the context of the jellium model [2]. Our results are in good agreement with other works which use a different method [3].

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ELECTRONIC STRUCTURE OF SILICA, CONTRIBUTION OF MANY-BODY CORRECTIONS

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The optical, electronic and structural properties of silica have been measured and studied extensively by experimentalist. It is well known that structural disorder form localized states within the band tails of electronic states, changing optical and electric transport processes in amorphous materials. Therefore, the kind and amount of the disorder is crucial to control physical properties of amorphous solids. However, in amorphous silica recent experiments seems to show that the static disorder do not contribute mainly to the absorption edge, contrary to the common sense. In this work, we go beyond the previous studies by using the Many-Body Perturbation Theory within the GW approximation for the calculation of quasi-particle band structures. We have performed such calculations on different silica glass models, and on defective silica (oxygen interstitials, silicon vacancies and danglig bonds). Our results show that the electronic properties of a-SiO2 are closer to those of its crystalline polymorphs, than those predicted by traditional mean-field pictures. Quasi-particle band structure have been calculated using the SaX package.

Oxygen vacancies in monoclinic tungsten oxide

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Abstract

The study of oxygen vacancies in the monoclinic tungsten oxide (WO_3) was performed within the framework of the self-consistent first-principle SIESTA method. This work revealed that the neutral oxygen vacancies were anisotropic with a strong correlation to the structural anisotropy of the WO_3 monoclinic room temperature phase. We showed that most of the structural relaxation around the vacancies occured along a single chain of W–O–W bonds and that the lowest energy corresponded to the formation of vacancies along the [001] crystallographic direction, where long and short W–O bonds alternate. Moreover, vacancies formation leads to the partial filling of the conduction band, in which 5d electronic states of the nearest neighboring W atoms of vacancies dominate. In term of Mulliken population the initial charge carried by the removed oxygen atom is mainly recovered on the O and W atoms closest to the vacancy.

The Structure of Methylthiolates on Au(111) Surface: a Combined Theoretical and Experimental Study

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Self-assembled monolayers (SAMs) of sulphur containing organic molecules on gold have received enormous attention due to the central role these interfaces play in molecular electronic devices, biosensors, surface coatings and nanolithography. We have resolved the controversy surrounding the $(\sqrt{3}\times\sqrt{3})$R30° structure of SAMS of methylthiolate on Au(111) by first principles molecular dynamics simulations, energy and angle resolved photoelectron diffraction and grazing incidence X-ray diffraction. Our simulations find a dynamic equilibrium between bridge site adsorption and a novel structure where 2 CH_3S radicals are bound to an Au adatom that has been lifted from the uppermost layer of the gold substrate. As a result, the interface is characterized by a large atomic roughness with both adatoms and vacancies. This result is confirmed by extensive photoelectron and grazing incidence X-ray diffraction measurements.

Effect of molecular structure on the visible light activity of dye sensitizers

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DFT calculations have been performed to investigate the molecular structure and electronic properties of perylene diimide (PDI) derived dye complexes based on projector augmented wave (PAW) method including gradient corrected exchange–correlation effects. Light harvesting properties of these molecules have been systematically studied by attaching different carboxylic acid groups and halogen atoms to PDI skeleton. We observed that the atomic size and electronegativity of the halogen alters the relaxed molecular geometries which in turn influence the electronic behavior of the dye molecules. The halogen atom and the ligands have significant effect on the ground state molecular structure of isolated dye molecules which are considered in this work. Our calculations revealed that the carboxylic acid ligands did not play an important role in changing the energy gap of the sensitizer. However, they serve as anchor between the PDI and possible substrate TiO_2 surface in a solar cell or photocatalyst application. Ruthenium bipyridine $[Ru(bpy)_3]^{2+}$ (RuBpy), a commercially available dye-sensitizer, was also studied for electronic and structural properties in order to make a comparison with PDI derivatives for light harvesting properties. The results suggest that fluorinated, chlorinated, brominated, and iyodinated PDI compounds can be useful as sensitizers in solar cells and in artificial photosynthesis.

AB-INITIO FOR A BETTER WORLD: case studies for hydrogen storage

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The necessity to environmentally friendly satisfy the demand of energy in the World has lead to increasing interest in the use of renewable and clean sources of energy. One of the promising options is the so called hydrogen economy, where the energy carrier is based on hydrogen and its use in fuel cells to produce energy, giving as a final product, just water. Besides it is very attractive idea, there are several important issues to be solved, such as the hydrogen production and storage. Density functional theory (DFT) is playing an important role in searching for and characterizing promising hydrogen storage systems. In this work, we have applied full range of first-principles characterization and optimization techniques to predict and calculate the structure, energetic, phase stability, thermodynamics and kinetics of novel hydrogen storage materials. We will present two distinct cases studies. One where the hydrogen is physically absorbed (inorganic nanotubes) and in the other extreme, where the hydrogen is chemically bonded in the system (ammonia-borane). Both systems represent a challenge for their computational modeling. Most inorganic nanotubes have radii greater than 10 nanometers. This size requires a cell of several hundred atoms, which is still computationally prohibitive. An alternative to treat the local properties of the nanotube, it is to use a novel method where the curvature of the nanotube is kept constant. In this case, much less atoms are needed, and the variation of the hydrogen energy binding with several radii can be addressed. For ammonia-borane, the enthalpies of the hydrogen release reactions for all decomposition products reported experimentally have been determined by including the zero point energy and finite temperature effects. Those results provide important information about the regeneration process of ammonia-borane complexes. In addition to this, by using Metadynamics, the mechanism and kinetic barriers for the release hydrogen and the rotation of the molecules in this system has been elucidated and calculated.

Ab-inito and Experimental ^{1}H NMR Signatures of Solvated Ions: H_3O^+, $H_5O_2^+$ and $Cl^- \cdot H_2O$ in HCl (aq)

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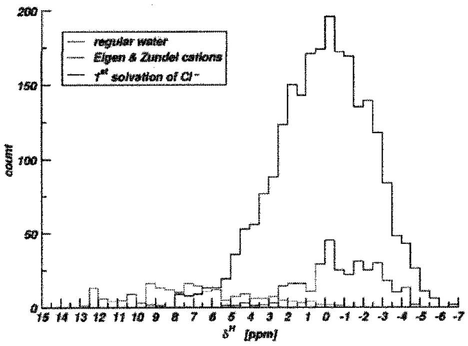
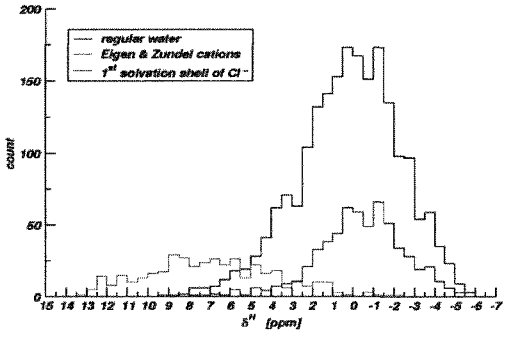
We present a combined experimental and ab-initio study of the ^{1}H NMR chemical shift resonance of HCl aqueous solution as a function of acid concentration, based on Car-Parrinello molecular dynamics simulations and fully periodic NMR chemical shift calculations. The agreement of average chemical shifts (computed values versus experimental ones) is very good. To clarify the origin of the obtained chemical shift distributions, we decompose the set of ab initio proton shifts into contributions from different types of geometrical configurations: Eigen and Zundel complexes, the first solvation shells of the Cl^- ions, and the regular water molecules. Finally, we analyze and discuss the computed histograms of instantaneous ^{1}H NMR chemical shifts in term of calculated individual NMR chemical shift signatures of solvated species. We show that the individual contributions of Eigen and Zundel cations, regular water molecules and the chlorine solvation shell to the NMR resonance line are very distinct, and almost independent on the acid concentration.





The very good agreement with experiment provides support that the description of disordered and highly fluctuating liquids and solutions by means of Car-Parrinello molecular dynamics simulations as well as the ensemble averages of spectroscopic parameters based on them do give a realistic picture of microscopic structure of complex solutions.

First Principles Calculation of Scattering of n-type carriers in $Si_{1-x}Ge_x$ Alloys

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(Dated: November 24, 2006)

First-principles electronic structure methods are used to find the rates of intra-valley and inter-valley n-type carrier scattering due to alloy disorder and phonon scattering in $Si_{1-x}Ge_x$ alloys. The required alloy elastic scattering matrix elements are calculated from the energy splitting of nearly degenerate Bloch states which arises when one average host atom is replaced by a Ge or Si atom in supercells containing up to 128 atoms. [1] The electron phonon interaction is calculated both from response function and frozen phonon calculations to obtain the deformation potentials, including alloy disorder using the Mass Approximation for the dynamical matrix. Scattering parameters for all relevant Δ and L intra- and inter-valley alloy and phonon scattering are calculated. Atomic relaxation is found to have a substantial effect on the elastic scattering parameters. f-type inter-valley scattering between Δ valleys is found to be comparable to other scattering channels. The n-type carrier mobility, calculated from the scattering rate using the Boltzmann transport equation in the relaxation time approximation, is in excellent agreement with experiments on bulk, unstrained alloys.

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Calculation of Phonon Dispersion Relations and Softening in Photoexcited Bismuth

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The phonon dispersion relations for equilibrium and photoexcited bismuth are calculated from first principles density functional perturbation theory, with constrained occupation of excited electronic states. The dependence of phonon frequency on photo-excited electron-hole plasma density is found for modes throughout the Brillouin zone. The resulting phonon dispersion curves are in good agreement with available neutron scattering data for the equilibrium occupation of electronic bands. We find the effect of phonon softening by the electron-hole plasma to be substantially larger in the optical modes than in the acoustic modes throughout the Brillouin zone.

Ab initio study of simple metal thin films

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Abstract

In this work, employing the density functional theory and ab initio pseudopotential method [1], we have studied the structural properties of simple metal thin films of Al, Na, and Cs. The slabs are taken in the [100] directions with different atomic layers of 3, 5, 7, 9, 11, 13, and 15. In these calculations, we have fully relaxed all the layers and obtained the work functions and surface energies. The results are compared with other works [2] and experiment [3].

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Ab initio calculation of the optical properties of the Si(113)3×2ADI surface

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The electronical and optical properties of the high-index (113) surface of silicon with the 3×2 ADI reconstruction have been investigated using ab initio methods. The groundstate calculations have been performed within the plane-wave pseudopotential approach to the density-functional theory as implemented in ABINIT [1]. The optical properties have been obtained from the matrix elements of the momentum operator using the TOSCA [2] package. First of all, we have investigated the electronic density of states and the electronic band structure where we assigned the surface and the bulk states. Here, have found a low-energy surface-located state with Tamm character. Furthermore, we inspected the localization of the relevant surface states. The optical properties, in our case, the reflectance anisotropy spectra (RAS), have been calculated. A layer-by-layer analysis yields the surface contribution of the spectra, which has initially been derived for the full slab. The states which are responsable for the surface peaks have been identified. In the discussion, also available experimental reference data have been taken into account.

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[2] `http://users.unimi.it/etsf`

First-principles study on electron conduction through thin oxide films

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Within the last several years, a large number of experimental and theoretical studies of ballistic electron conduction through nanoscale junctions such as quantized conductance or ballistic transport have been carried out. Future research on conduction properties can be expected to lead to new discoveries of nanoscience and novel fabrications of electronic devices. So far, we have developed the first-principles calculation method with the incorporation of the overbridging boundary matching formalism and the real-space finite difference approach to elucidate the relationship between geometrical structures and electron conduction properties in which nanostructures are suspended between two semi-infinite electrodes. We will present our computational procedure and the results of the following simulations. In this study, we examine the leakage current through the thin silicon oxide films using the newly developed methods. The computational models consist of a silicon dioxide film and a silicon substrate sandwiched between semi-infinite jellium electrodes. In addition, some of the models contain defects at the interface between the silicon dioxide and the silicon substrate and also in the silicon dioxide film. First, the electronic structures of these systems with and without external electric fields which imitate gate bias were explored. In the case of the models including defects, the electronic states owing to the defects are observed at the Fermi level and the significant percolations of the charge density distributions around the Fermi level into the silicon dioxide films are observed when the external electric fields were applied. We then examined differential conductance as a function of the bias voltage and found that the peaks of the leakage current correspond to the energy of the defect states. The resultant leakage current of the model with the defects is ten times larger than that of the model without the defects. What is more, the contribution to the leakage current of the defect in the film is larger than that of the defect at the interface.

Nonthermal broadening in the zero bias conductance of double quantum dots

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We calculate the exact temperature dependence of single level and double level line shapes. We show analytically that a non-thermal broadening of line shapes occurs for serially coupled double dot systems. We also present numerical confrmation of this effect using a tight binding simulation of a double dot structure.

Unravelling the mechanism of phase change materials : an *ab initio* MD study

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Nowadays, thin layers of phase change materials are commonly used in rewritable DVD's and as PC-RAM. The writing process is achieved by a first local melting of the crystalline phase through a laser pulse (DVD-RW), or by Joule heating (PC-RAM), followed by a fast amorphization. Reading is then possible thanks to the large differences in optical reflectivity and electrical conductivity between the two phases. The erasing process is achieved through moderate heating of the amorphous phase and recrystallization. Despite their every day use, the internal mechanism responsible for the phase-change behavior of these materials remains controversial and theory is lacking.

Among phase change materials, the $Ge_2Sb_2Te_5$ compound is one of the most successfully used in applications. Currently accepted models [1, 2] are based on X-ray absorption measurements and suppose a complete reorganization of bonds during amorphization, with Ge atoms changing from sixfold to tetrahedral coordination.

In this study, we perform ab initio molecular dynamics simulations of the $Ge_2Sb_2Te_5$ liquid phase at 1073K and obtain an excellent agreement with the experimental structure factor. Twenty individual, uncorrelated, liquid atomic configurations are then fully relaxed, both for the ionic and cell degrees of freedom. The relaxed structures are then used as model amorphous structures and their EXAFS signature is positively compared with the experimental spectra. The computed electrical conductivities of the three phases (cubic solid, liquid and relaxed structures) prove to be very different, accordingly with the experiment. As a conclusion, we invalidate the commonly accepted model and show that Ge atoms remain octahedrally coordinated in the amorphous phase, with 6 very unequal first neighbors distances.

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Formation and segregation energies of doped nanowires

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Nanowires (NWs) are one-dimensional nanostructures, that have generated a lot of scientific interest as possible building blocks for nanoscale devices. Recent experimental results have already shown applications of NWs as electronic devices, including FETs[1], p-n diodes[2], bipolar junction transistors[3] and as chemical and biological sensors[4]. Important properties can be controlled during synthesis by doping.

We performed a detailed *ab initio* study of B and P doped and BP codoped Si nanowires, oriented along the [110] direction. The localization of the dopants and their formation and segregation energies were studied and we found that the B and P dopants will migrate to the edge of the wire and that the formation energy for codoping is smaller than for the single doped cases.

Because these thin wires have a large surface to volume ratio, the number of dangling bonds can be larger than the number of dopants. These defects have a substantial effect on the formation and segregation energies. The P dopants are more easily trapped than B dopants and become electronically inactive. Similar calculations were performed on Ge NWs.

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Structural and electronic properties of defected carbon nanocapsules

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Abstract

Structural and electronic properties of defected carbon nanocapsule systems have been investigated theoretically by performing semi-empirical molecular orbital and density functional theory methods. Geometries of the structures have been optimized by applying PM3 level of calculations within restricted Hartree Fock formalism and electronic information have been obtained by applying B3LYP level of density functional theory calculation using 3-21G basis set. The studied systems include (5,5) and (9,0) single-walled carbon nanocapsules with mono atom vacancies and Stone-Wale defects. Molecular dynamics simulations have also been performed to study the structural properties and energetics of the defected structures.

Ex nihilo determination of structures by random searching

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We introduce a search strategy for predicting structures based on relaxation of randomly chosen structures under the forces and stresses obtained from *ab initio* electronic structure computations. By starting from random structures we aim to obtain a wide coverage of the "structure space", which allows for the possibility of finding radically new structures which have not been considered previously. Our search strategy is remarkably straightforward and does not require the selection of highly-system-specific parameter values.

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.

We illustrate the performance of the method with applications to silane [1], self-interstitial defects in silicon and other systems. It has recently been suggested [2] that the group IV hydrides, such as silane (SiH_4), might become metallic at pressures achievable in diamond anvil cells because the hydrogen in these materials is "chemically precompressed" by the presence of the group IV atoms. Such metallic phases would be expected to have many high-frequency phonon modes, suggesting they might exhibit phonon-mediated high-temperature superconductivity. Feng *et al.* [3] reported *ab initio* density-functional-theory (DFT) of silane structures under pressure indicating that metallisation occurred at 91 GPa. Our search strategy produces structures which are significantly more stable than those of Feng *et al.*, and we find metallisation at much higher pressures, although still within range of diamond anvil cells. Recently, Sun *et al.* [4] reported evidence for a transition from an insulator to a semiconductor between 92 and 109 GPa, but no evidence of metallisation up to 210 GPa, which is consistent with our results.

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Ab-initio study of the structural and vibrational properties of TeO_2-based glasses

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TeO_2-based glasses are promising active materials for optical fiber amplifiers due to their large cross section for stimulated Raman scattering [1]. These properties are influenced by doping agents such as Na_2O or WO_3 added to improve the stability of the glass towards recrystallization. Despite the technological interest of these materials, the dependence of the microscopic structural properties and Raman response on doping is largely unknown. To address this issue we have performed ab-initio calculations on the structural and vibrational properties of the known crystalline phases of TeO_2 (α, β, and γ) and of tellurite glasses pure and doped with WO_3. The glass models, containing up to one hundred atoms, are generated by quenching from the melt within ab-initio molecular dynamics simulations. The calculated structure of the pure glass compares well with neutron diffraction data [2]. Moreover, Raman and IR spectra calculated within density functional perturbation theory [3,4] are in good agreement with available experimental data for crystalline and amorphous TeO_2 phases and allow us to identify in the glass spectrum the vibrational modes responsible for the most intense Raman peaks. Conversely, large discrepancies between the experimental and theoretical Raman spectra are found for TeO_2-WO_3 glass that we have modeled by a solid solution. Comparison between experimental Raman spectra of TeO_2-WO_3 glass and WO_3 nanoparticles [5] suggests the possible formation of WO_3 amorphous nanostructures in real TeO_2-WO_3 samples.

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Structural and dynamical properties of a confined room temperature ionic liquid

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Room temperature ionic liquids (RTIL) have drawn significant attention during the past years due to their low vapor pressure, high density of charge carriers and high viscosity coefficients [1]. Because of these factors, they have emerged as an alternative electrolyte for dye sensitized solar cells (DSSC) [2]. In a DSSC a dye-coated semiconductor (TiO_2) layer forming a nanoporous network collects electrons from the photoexcited dye molecules. The dye is then regenerated via electrons donated by a redox couple (I^- / I_3^-), which is dissolved in a RTIL. This redox-electrolyte system has to penetrate the porous matrix in order to accomplish the dye regeneration process. It is known experimentally that this process is fast despite the confinement and the significant size of the RTIL components [2]. In this work we study, using molecular dynamics simulations, the behaviour of the RTIL dymethilimidazolium chloride confined between to flat walls at different confinement widths. In addition, the response of this confined liquid to an external electric field, such as that created by the charged TiO_2 nanoparticles, is presented. The response of the liquid is analyzed in terms of mass and charge density fluctuations. As a result, we find that the dynamics of the confined RTIL can be described in terms of two regimes: a fast process (faster than 1ps) that involves mainly a small re-accommodation of the anions, and a much slower process corresponding to structural relaxation. We compare linear response calculations with non-equilibrium molecular dynamics simulations of the confined liquid when an applied external electric field is suddenly switched off.

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Optimized Effective Potential Method: extension to non-collinear magnetism and current density

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Explicitly orbital-dependent approximations to the exchange-correlation energy functional provide a natural approach to treat non-collinear magnetism in spin-density functional theory (SDFT). Moreover, they are also well-suited to overcome practical problems of LDA-type approximations in current-SDFT (CSDFT). In order to deal with orbital functionals in practice the so-called Optimized effective Potential (OEP) method is usually employed. Here we present the extension of the OEP method to non-collinear SDFT and CSDFT. We suggest a simplifying approximation in the spirit of the well-known approximation by Krieger, Li, and Iafrate (KLI), but we also propose a practical scheme for the full solution of the resulting integral equations for the exchange-correlation potentials. We analyze these equations and present numerical results for atoms, quantum dots, and solids.

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One- and two-photon absorption of carbon nanotubes

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We present a first-principles study of the optical properties of single-walled carbon nanotubes (SWCNT). We employed many-body theoretical methods to determine the excited states of the system. Both self-energy corrections in the treatment of single-particle energies and effects arising from the electron-hole interaction are included in our calculations [1-2]. Our symmetry-based approach exploits all the symmetries of these systems, making feasible the study of large tubes which are otherwise impossible to treat in standard approches within the many-body framework. In addition, this picture gives a more complete understanding of the excited state properties, of the degeneracies and group character of the single-particle bands, and of the selection rules involved in determining optical spectra. We computed one- and two-photon absorption spectra, achieving excellent agreement with recent experiments [3-4]. We found that many-electron effects are crucial in both the peak shapes and positions for all the tubes studied. In particular, for 0.4-0.8-nm-diameter tubes, the calculated exciton binding energies range between 0.3 and 0.9 eV, showing important excitonic effects even in large diameter nanotubes. Our theoretical analysis, in conjunction with combined one- and two-photon experiments, allows one to estimate of the binding energy of excitons.

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Spin waves in Mn-doped Si: exchange interactions from first-principles calculations

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Abstract

There has been considerable interest in magnetic semiconductors in recent years for potential applications in the field of spintronics. The present work was motivated by the recent experimental achievement of above-room-temperature magnetism in Mn doped silicon (Phys. Rev. B **71**, 033302 (2005)). We present the results of Density Functional calculations that have been carried out to determine the strength of the distance-dependant exchange interaction in Mn-doped Si. The exchange interaction determines the energy difference between ferro-magnetic and anti-ferromagnetic spin configurations and as such it provides for a prediction of spin-wave velocities. Such spin waves, if they exist, are of interest in that they may provide a means for transmitting spin-based information. The calculations were carried out as follows. In a 64-atom unit cell of Si we constructed a series of configurations in which a pair of Mn atoms substitutes for a pair of Si atoms. The magnetic moments of the Mn atoms were constrained to assume a ferromagnetic configuration on the one hand and an anti-ferromagnetic configuration on the other. Comparison of the relative energy differences for a series of Mn locations yielded the distance dependant exchange interaction J(R). Interestingly we find that the exchange interaction is negative (anti-ferromagnetic) for short and long distances and is positive (ferromagnetic) for intermediate distances. This poster will present these findings along with estimates of spin-wave velocities, densities of states, band structure and spin-density distributions.

Symmetry breaking in a dense liquid: Why sodium melts at room temperature

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The melting curve of sodium measured in [1] exhibits unusual features under pressure : the melting temperature, Tm, reaches a maximum around 30 GPa followed by a sharp decline from 1000 K to 300 K in the pressure range from 30 to 120 GPa. In this study, the structural and electronic properties of molten sodium are studied using first principles theory. With increasing pressure, liquid sodium initially evolves by assuming a more compact local structure, which accounts for the maximum of Tm at 30 GPas. However, at pressure around 65 gigapascals a transition to a lower coordinated structure takes place, driven by the opening of a pseudogap at the Fermi level. Remarkably, the broken symmetry liquid phase emerges at rather elevated temperatures and above the stability region of a closed packed free electron-like metal. The theory explains the measured drop of the sodium melting temperature, down to 300 kelvin at 105 GPas.

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A generalized Sham-Schlüter equation: the link between nonlocality and frequency dependence

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We present an in principle exact approach to construct effective potentials and kernels for the calculation of electronic spectra. In particular, the potential that yields the spectral function needed to describe photoemission turns out to be dynamical but local and real. Using explicit examples we illustrate how the nonlocality of the physical self-energy is converted into a frequency dependence of the effective potential. We also show that our approach leads to a very short derivation of a kernel that is known to well describe absorption and energy-loss spectra of a wide range of materials.

Ab-initio calculation of STM images of PTCDA:Ag(111) and of Si(111)-(2x1)

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We discuss the calculation of STM images on the basis of ab-initio electronic-structure theory, employing the approach of Tersoff and Hamann. One of the key ingredients is the careful evaluation of electronic wave functions up to 10 Angstrom outside the surface. To this end, we calculate each wave function close to the surface, take its two-dimensional Fourier transform, and extrapolate each Fourier component to the height of the tip, allowing to evaluate the LDOS and resulting tunneling current at the tip position. In the case of the Si(111)-(2x1) surface the two dangling-bond surface bands lead to high-contrast STM features with characteristic spatial shifts between both bands, as we also observe in experiment [1]. In the case of a monolayer of PTCDA on Ag(111), high-resolution images are obtained in theory and experiment, as well, allowing for an accurate determination of adsorption sites and for a systematic comparison between theory and experiment regarding trends with varying tip height and voltage [2].

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New Carbon-Nitride (C_3N_4) Nanocluster Structures

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We have studied, by first principles density functional calculations, carbon-nitride cagelike clusters. Firstly, we are interested in clusters which keep C_3N_4 stequiometry and whose facets preserve the same structure as the graphitic form: a "benzenic ring" (C_3N_3) joined by Nitrogens (N) with coordination of 3. We propose much smaller structures, up to a little more than 1 nm, than those previously reported in literature, with a small number n of C_3N_4 units. All the presented structures have been relaxed by force minimizations and their stabilities have been tested. In order to explain all the experimental results, small variations in the stequiometry were used to build new clusters.

Electronic decoupling in mechanically connected nanowire arrays

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We perform first-principles and empirical electronic structure calculations demonstrating a novel approach to quantum confinement for the engineering of one-dimensional nanostructure fabrication with no need of catalyst agents. The method is based on a lithography design of a pattern of channels onto a conveniently cleaved semiconductor surface. We show that when the channel diameter is sufficiently larger than the interstitial space, the resulting pillars constitute an ordered array of electronically independent, though mechanically interconnected nanowires.

We also prove that a controlled coupling of the nanowires can be achieved, as long as one is capable to tune, at fabrication time, the thickness of the interconnections, which are ultimately responsible of the efficiency of the quantum confinement. This method, being based on a top-down approach, would yield an ensemble of identical nanowires, grown along the same crystallographic orientation and with similar properties concerning the length and the diameter. The dispersive behaviour is conclusively determined from the observation of the band width for the bands of interest and from the calculation of the relevant effective masses.

The use of such structures could be easily extended to quantum well or superlattice substrates, e.g. GaP/InGaAs or GaAs/AlGaAs, leading to the fabrication of one-dimensional heterostructures or quantum dots with potential applications as light emitting devices.

Cu-based metalorganic systems: an *ab initio* study of the electronic structure

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Within a first principles framework, we study the electronic structure of the recently synthesized polymeric coordination compound Cu(II)-2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene (CuCCP), which has been suggested to be a good realization of an antiferromagnetic Heisenberg spin-1/2 chain. By using a combination of classical with *ab initio* quantum mechanical methods, we design on the computer reliable modified structures of CuCCP aimed at studying effects of Cu-Cu coupling strength variations and dimensional crossover on this spin-1/2 system. For this purpose, we performed two types of modifications on CuCCP. In one case, we replaced H in the linker by i) an electron donating group (NH_2 and ii) an electron withdrawing group (CN), while the other modification consisted on adding H_2O and NH_3 molecules in the structure which change the local coordination of the Cu(II) ions. With the downfolding method within the framework of N-th order muffin-tin orbital technique (NMTO-downfolding) we provide a quantitative analysis of the modified electronic structure and the nature of the Cu-Cu interaction paths in these new structures and discuss implications for the underlying microscopic model. This study shows that such a designing procedure has important predictive power for interesting hypothetical systems to be synthesized in the laboratory.

Effects of the proteic environment on the electronic density of dihydrofolate reductase substrates

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The enzyme dihydrofolate reductase (DHFR) reduces 7,8-dihydrofolate (DHF) to 5,6,7,8-tetrahydrofolate with high specificity, and folate to DHF, in a less efficient side reaction. Density functional studies at the LDA level of theory point to a significant role of protein-induced polarization on the observed selectivity [1]. However, Moller-Plesset (MP) calculations are less conclusive [2], resulting in electronic density variations upon binding of the substrates to the enzyme about one order of magnitude lower than in LDA calculations. Both approaches were limited, however, to a small number of atoms in the active site, with the rest of the protein represented as a set of point charges.

We used a linear-scaling DFT method, as implemented in our code Conquest [3], to extend the models to the substrates and about 20 amino acids surrounding the active site of DHFR. All systems were globally neutral, but charged amino acids were present. Our LDA calculations led to density changes of the order of those found in MP results, but variations were localized on the correct protonable nitrogens. Furthermore, the influence of the conformation of a flexible loop, known as Met20, was also demonstrated, in agreement with experiments.

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Order-N First-Principles Electronic Structure Calculations in Inhomogeneous Semi-Infinite Systems

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abstract

For the strict and detailed theoretical predictions of the electronic structures of a system in which nanostructures are connected to semi-infinite bulks, the elimination of artifacts and accurate modeling of the system are indispensable. We present a new approach which is free from these problems. Our procedure is based on the realspace finite-difference (RSFD) method and the direct minimization of the energy functional proposed by Mauri, Galli and Car (MGC). The RSFD methods allow us to impose arbitrary boundary conditions on models and to introduce spatially localized orbitals easily. By combining the RSFD method with the MGC energy functional, the self-consistent ground-state electron-charge densities of nanostructures attached to semi-infinite crystalline bulks can be obtained satisfactorily.

Nuclear quantum effects on NMR parameters from ab-initio simulations in the condensed phase

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NMR parameters, such as NMR chemical shifts and nuclear quadrupole coupling constants (NQCC) have been shown to be very sensitive to structural and dynamical effects. A combined approach of molecular dynamics simulations and calculations of spectroscopic properties recently revealed a significant change of the NQCC with temperature [1] in systems that are strongly hydrogen bonded. Since NMR is probing the vicinity of a nucleus via the nuclear spin, the measured quantities should also be sensitive to quantum effects of the nucleus that are not included in the commonly used Born-Oppenheimer approximation.

We are using the path integral formalism as implemented in CPMD [2] for simulating nuclear quantum effects in the condensed phase. The impact on NMR parameters is expected to be especially pronounced if tunneling occurs, i.e. the quantum nature of the nuclei is important for understanding the system. Thus we have investigated molecular structures with short hydrogen bonds (benzoic acid) and potential candidates for tunneling phenomena (phthalocyanines).

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Nuclear quantum effects in the structure of solids: a model study

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Abstract

Ab initio electronic structure calculations constitute an important tool in predicting physical and chemical phenomena in atoms, molecules and solids. This way to tackle the problems is based on the following approximations: (a) the adiabatic separation of nuclear and electronic degrees of freedom, (b) the classical treatment of atomic nuclei, and (c) various approximations for the electronic exchange and correlation.

The classical nuclei approximation works reasonably well in heavy nuclei systems. However, when dealing with systems containing light atoms like H, it is necessary to take into account the quantum nature of the nuclear degrees of freedom. Hydrogen-bonded systems constitute an example where the quantum nuclei play a crucial role. In fact, for Potassium dihydrogen phosphate (KH_2PO_4, or KDP) crystals in the paraelectric phase at high preassure, the H-atoms occupy with equal probability two symmetrical positions along the H-bonds. At low pressures however, the protons localise into one of the symmetric sites, thus leading to an ordered ferroelectric phase. The critical pressure P_c for this phase transition depends strongly on the isotope. In fact, the deuterated compound (DKDP) exhibits a P_c about two times larger than KDP.

To describe atomic nuclei it is necessary to solve the nuclear Schrödinger equation in a multidimensional potential energy surface (PES). This 3N-dimensional PES (where N is the number of atoms) needs to be mapped, and this constitutes an immense computational task, especially for systems with many atoms. Adequate approximations are then desirable.

In this work (still in progress), a linear O-H chain model is discussed. The isotopic effect at zero temperature is studied as a function of the number of unit cells. The vibrational-self-consistent-field (VSCF) method (approximating the nuclear wavefunction with a product wavefunction in terms of vibrating coordinates) arises as a possible alternative for simplifying the problem.

Interaction of a CO molecule with a Pt monatomic wire

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Recent experiments showed that the ballistic conductance of Pt nanocontacts is strongly modified by CO adsorption.[1] We present first principle calculations, based on density functional theory, of the interaction between a monatomic Pt wire and a CO molecule placed on top of one Pt atom. The results obtained by using scalar-relativistic (SR) and fully relativistic (FR) ultrasoft pseudopotentials are compared and the effect of spin-orbit coupling on the interaction is highlighted. In both cases, a chemical bond is seen between the molecule and the Pt wire, although with a small net charge transfer from the molecule to the wire. The interaction is due to the 5σ (HOMO) and to the doubly degenerate $2\pi^\star$ (LUMO) CO orbitals, which are involved in a donation-backdonation process similar to that seen for CO adsorbed on transition-metal surfaces. We discuss the symmetry of the electronic states in the SR and FR cases and we show that the inclusion of the spin-orbit coupling, while changing the electronic structure of the wire, does not modify substantially the interaction between the molecule and the wire.

In the SR case, the ballistic conductance of the system is calculated with the method introduced in Ref.[2]. We find that the adsorption of the molecule on the nanowire reduces the conductance from 8 e^2/h to about 6.1 e^2/h. Actually, in this geometry, only the conductance of the s and d states that interact with CO is reduced, the other states are almost perfectly transmitted. The study of the adsorption in a bridge configuration and the calculation of the FR conductance are presently in progress.

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Proton momentum distributions in hydrogen bonded systems from ab-initio path integral simulations

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We present a modification of the path integral implementation in the CPMD package suitable for the calculation of nuclear momentum densities $\rho_n(\mathbf{p}) = |\Psi_n(\mathbf{p})|^2$ where $\mathbf{p}$ and Ψ_n are the nuclear momentum and the nuclear rovibrational wavefunction. The implementation is tested on protons in small molecules where $\rho_n(\mathbf{p})$ can be calculated analytically within the harmonic approximation.

Experimentally, the momentum distributions $\rho_n(\mathbf{p})$ are directly accessible through Neutron Compton Scattering (NCS) methods. We apply our path integral technique to strongly hydrogen bonded systems in the condesed phase at different temperatures in order to characterize tunneling phenomena.

Quasiparticle Calculations of Band Offsets of Silicon with high-κ dielectrics

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The size reduction of MOS transistor requires the usage of high-dielectric materials to replace SiO_2 as gate oxide layers. As the high-κ/Si interface is formed, it is crucial that the band offsets be large enough to prevent electron or hole injection. In this study we have used first-principle DFT calculations within the local density approximation to study the band offsets of SiO_2/Si and $ZrSiO_4$/Si. We have included many body corrections as calculated by GW approximation. Indeed we have examined the capability of the quasiparticle corrections to predict the band offsets for a well known system as SiO_2/Si. The calculated band discontinuities were found to be in a good agreement with the experimental results.

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Interfacial water on the Cl-Si(111) and H-Si(111) surfaces from first principles calculations

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Abstract

Interfacial water on the Cl- and H-terminated Si(111) surfaces is investigated using a first-principles approach. The interaction of water with both substrates is found[1] to be significantly weak, although bonding with the Cl-Si(111) surface is relatively stronger, due to the electrostatic contribution. According to a molecular picture for attributing the hydrophilic/hydrophobic character, both surfaces should be considered as hydrophobic, at variance with the interpretation of recent experiments[2] which seems instead to support the hydrophilic nature of the Cl-Si(111) substrate.

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Electronic Structure in Silicon Clathrate Nanowires

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We investigate two types of Si clathrate nanowire which have recently been proposed [1,2] to be more energetically stable than the conventional tetrahedral structure of Si. Silicon clathrate nanowire consists of 34 and 46 atoms in the unit cell. The clathrate material has a nano-cage structure and we have shown that for both types of clathrate nanowire, it is possible for an alkali impurity to be encapsulated at the centre of the cage. We have analysed the electronics structure of the clathrate and found that the pure clathrate nanowire formed without any impurity has a band gap and therefore behaves as a semi-conductor. However, in the presence of impurities the electronic properties of the clathrate nanowires change dramatically and can become conductors.

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Linear-Scaling Plane Wave Density Functional Theory with the ONETEP program

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The ONETEP [1] program for density functional theory (DFT) calculations with linear-scaling computational cost will be presented. The linear-scaling is achieved by using a reformulation of DFT which takes advantage of the exponential decay of the density matrix in systems with a gap (e.g. molecules, semiconductors and insulators). The method uses a plane wave basis set which affords high accuracy that can be controlled in a systematic manner and also offers other important advantages such as uniform description of space and lack of basis set superposition error. Examples of calculations with ONETEP will be presented.

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Magnetic phenomena and ballistic transport in Pt nanowire contacts(*)

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We present a first-principles DFT study of the electronic structure, magnetic properties, and ballistic electron transport in short monatomic Pt nanowires between two semi-infinite Pt leads. Both scalar relativistic (SR) and fully relativistic (FR) (including spin-orbit effects) calculations are carried out and compared. First, we consider an idealized infinite tipless Pt nanowire. Here, FR calculations yield a ferromagnetic ground state (with the magnetization parallel to the wire) already for the unstressed wire [1,2], while SR calculations predict the nanowire to be nonmagnetic. Next, we found that very short 3-atom and 5-atom stressed wires remain locally magnetic even in contact with macroscopic nonmagnetic Pt leads, with the magnetization parallel to the wire axis, owing to orbital magnetism. Ballistic conductance of these nanocontacts is calculated using the scattering-based method [3]. Preliminary results indicate a ballistic conductance for a stressed 5-atom wire of about 2.0 G_0 ($G_0 = 2e^2/h$ is the conductance quantum) for parallel magnetization, 2.3 G_0 for perpendicular magnetization, and 2.4 G_0 in the nonmagnetic case. The former is in closest agreement with experimental values reported in break junctions [4].

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Adsorption of thiophene on Cu(110) and Cu(110)-(2x1)O

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Various oligomers have come up as potential candidates for both, electronic and opto-electronic devices like OFETs, OLEDs, *etc.* Such applications are usually based on thin films grown on top of metal substrates. Due to the anisotropy of these materials one of the major questions in this context is, how the molecules are arranged on the surface. From the theoretical point of view, mainly the bulk properties of oganic molecular crystals have been studied, while thin organic films, their terminations, and interfaces are hardly explored. In the present work, we perform density-functional calculations to study the relaxation and orientation of organic molecules on metallic surfaces. To this extent, we first investigate the relaxation of the pure Cu(110) and the Cu(110)-(2x1)O surfaces. In a next step, we study, how a molecule is adsorbed. In this presentation, we will mainly focus on thiophene, where the adsorption energy corresponding to various positions and orientations of the molecule is calculated on the search for the most favourable adsorption site. Thereby we focus on the role of the exchange-correlation potential including van der Waals interaction. We also address the question, how sensitively the adsoption energy depends on surface relaxation effects.

Magnetic circular dichroism and the orbital magnetization of ferromagnets

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The spontaneous magnetization of ferromagnets has both spin and orbital contributions, $\mathbf{M} = \mathbf{M}_{\rm spin} + \mathbf{M}_{\rm orb}$, which can be separated out via gyromagnetic measurements. Recently[1] it was found that, when expressed as a bulk property of the Bloch electrons, the orbital magnetization itself consists of two terms, $\mathbf{M}_{\rm orb} = \widetilde{\mathbf{M}}_{\rm LC} + \widetilde{\mathbf{M}}_{\rm IC}$, which can be loosely interpreted as the localized and itinerant contributions, respectively. Interestingly, $\widetilde{\mathbf{M}}_{\rm LC}$ and $\widetilde{\mathbf{M}}_{\rm IC}$ are separately gauge-invariant, which raises the possibility that they may be independently measurable. We show that indeed they are related to the magnetic circular dichroism (MCD) spectrum by a subtle sum rule. MCD, the difference in absorption between left- and right-circularly-polarized light, is given by $\sigma^{(2)}_{{\rm A},\alpha\beta}(\omega)$, the absorptive part of the antisymmetric conductivity. We derive the following sum rule for the interband contribution: $\int_0^\infty \vec{\sigma}^{(2)}_{\rm A}(\omega)d\omega = (2\pi ec/\hbar)(\widetilde{\mathbf{M}}_{\rm LC} - \widetilde{\mathbf{M}}_{\rm IC})$, where $\vec{\sigma}^{(2)}_{\rm A}(\omega)$ is a pseudo-vector. Hence, by combining the results of gyromagnetic and magneto-optical experiments, $\widetilde{\mathbf{M}}_{\rm LC}$ and $\widetilde{\mathbf{M}}_{\rm IC}$ can in principle be measured independently.

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Molecular modeling and simulation of PPV oligomers: Ground and excited state dynamics of isolated and stacked chains in the gas phase.

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The ground and excited state dynamics of poly(p-phenylenevinylene) (PPV) chains is studied through quantum/classical molecular dynamics simulations. The model used in the simulations combines the semiempirical Pariser-Parr-Pople (PPP) Hamiltonian to threat the π molecular electronic structure with a flexible mechanical force field for the classical nuclear degrees of freedom. We first simulated PPV chains of various length in the ground state. The absorption spectra show saturation with the increase of the chain length and we deduce a conjugation length of about 10 units in very good agreement with experiments. The thermal contribution to the broadness of the first absorption band is estimated to be 0.2 ev at T=300K. In order to investigate the relationship between the emission and chain conformation we simulated an isolated chain of (10)PPV in the ground and the lowest excited state. The emission spectrum, redshifted with respect to absorption of about 0.2 ev as found in experiments, shows a structured line-shape that is generally related to the vibronic contributions of the CC double bond stretching, and that we relate to the photoinduced CC bond distortions. Actually, the exciton self-traps in the middle of the chain inducing a change of the bond lengths. The magnitude of such distortions agrees with the results from other theoretical methodologies: the maximal shift, occurring in the central vinylene junction, is $\simeq 0.034$ Å. The characteristic time for the bond relaxation after photoexcitation is shorter than 100 fs; and the relaxation is guided by a compensatory release of energy from the double to single bonds in the vinylene junctions and p-phenyl rings, respectively. Finally we simulated a pair of stacked (5)PPV chains. The chains pack at a contact distance of 3.6 Å and slide one along the other with a characteristic time of about 10-15 ps. The absorbtion spectrum peak arises from the electronic transition $S^0 \rightarrow S^2$ whereas the S^1 is a dark state. After photoexcitation in the S^2 the system decays non adiabatically in the lower excited state in about 10-50 fs. The non adiabatic coupling of this transition is in the order of 0.1-0.4 ev and is localized in the externals and central parts of the chains. The system does not make non adiabatic transition from the S^1 state toward the ground state. Therefore the luminesce of the system arise from the $S^1 \rightarrow S^0$ transition and is characterized by a small transition dipole.

CO adsorption on metal surfaces:
a hybrid density functional study with plane wave basis set.

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(Dated: November 30, 2006)

Abstract

We present a detailed study of the adsorption of CO on Cu, Rh, and Pt (111) surfaces in top and hollow sites. The study has been performed with a gradient corrected functional (PBE) and PBE0 and HSE03 hybrid Hartree Fock density functionals within the framework of generalized Kohn-Sham density functional theory using a plane-wave basis set. As expected, the gradient corrected functional shows the tendency to favor the hollow sites, at variance with experimental findings that give the top site as the most stable adsorption site. In contrast, the PBE0 and HSE03 functionals seem to reduce this tendency. Indeed, they predict the correct adsorption site for Cu and Rh surface but fail for Pt. But even in this case, the hybrid functional destabilizes the hollow site by 50 meV compared to the GGA description. This suggests that hybrid functionals give an overall better description of the chemisorption of CO molecules on metal surfaces, but, *in general*, they still do not predict the correct adsorption site for CO. The results of the total energy calculations are presented, along with an analysis of the projected density of states and Löwdin charges.

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Competing mangetic phases of Mn_5Ge_3 ferromagnetic compound.

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(Dated: December 1, 2006)

Abstract

Germanium-based compounds have recently attracted considerable attention in Semiconductor Spintronics. The Mn_5Ge_3 compound have been grown on Ge(111) substrate so that epitaxial "spin valves" can be fabricated. Recent experiments suggest a spin structure that is likely non–collinear. In order to gain deep insights into the magnetic structure of this compound, we have performed fully unconstrained ab–initio pseudo–potential calculations within spin density functional theory. We have considered several possible magnetic configurations: paramagnetic, Collinear (C) ferromagnetic (FM) and anti–ferromagnetic (AFM), Non–Collinear (NC) spin configurations. We first study the effect of the pressure. All the phases are degenerate for volumes smaller than 0.96 V_{eq}; for $V \simeq 0.96$ V_{eq}, the paramagnetic phase becomes unstable with respect to the other magnetic phases which are still degenerate among themselves. For $V \simeq 0.98$ V_{eq} the degeneracy between C-AFM and C-FM is removed (C-FM becomes stable), but C-FM and NC still remain degenerate. At equilibrium volume, the C-FM and NC self-consistent solutions (which have different magnetic states) are competing phases, suggesting the occurrence of *accidental magnetic degeneracy* also in Mn_5Ge_3 real samples. For $V \simeq 1.1$ V_{eq} there is a crossover of the C-FM and C-AFM curves, with the C-AFM becoming favourite with respect to C-FM for larger volumes; the NC phases is degenerate with C-AFM for $V<1.2V_{eq}$. For larger volumes, a complex competition between C-AFM and NC develops and the NC spin-configuration becomes the most stable one. Finally, we have studied the effect of strain field. Interestingly, the degeneracy of the NC phase with the C–spin configurations (FM and AFM) is definitely removed under the effect of uniaxial structural distortions (NC spin configuration is favoured under tensile uniaxial strain). We note that in a recent paper[1], it has been demonstrated that even in typical ferromagnetic materials (e.g., Fe) it is possible to stabilize the NC magnetic order in high pressure experiments. Our results show that even under uniaxial strain, the NC order can be stabilized with respect to C one.

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EQUATIONS OF STATE AND MELTING CURVE OF TANTALUM FROM FIRST PRINCIPLE CALCULATIONS

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ABSTRACT

A general description of lattice dynamics and thermal properties of body-centered cubic tantalum using finite temperature density functional theory (DFT) is presented. The approach works within the projector augmented wave implementation of DFT and explicitly treats in valence the $5p$, $6s$ and $5d$ electrons. The equation of state at zero temperature and the phonon dispersion are investigated using both the local density approximation (LDA) and generalized gradient approximations (GGA). Good agreement with the zero temperature equation of state and zero pressure phonon dispersions is obtained with GGA. We also report the full melting curve of Ta obtained with explicit coexistence simulations of solid and liquid, performed using an embedded atom model (EAM) fitted to ab-initio molecular dynamics simulations. The ab-initio melting curve is then obtained correcting the EAM results by calculating free energies differences between the EAM and the ab-initio potentials. Results are in good agreement with diamond anvil cell experiments at low pressure, but rapidly diverging from these as pressure is increased, and agreeing well with shock-wave experiments at high pressure.

Non-Adiabatic Molecular Dynamics Study of Conduction in Small Molecules

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One of the difficulties in understanding the operation and control of some molecular electronic devices is the complex dynamical interaction between the geometry, conductance and the local electrostatic potential of the molecule. This study employs a non-adiabatic, Ehrenfest formalism to investigate the effect of a steady-state current on the structure and electronic properties of a proposed molecular switch. Small oligo(phenylene-ethynylene) molecules are described by a transferable tight-binding scheme for hydrocarbons with full charge self-consistency. The molecular dynamics, featuring excited current-carrying states, was performed using the DINAMO code in a system with open boundaries. Dynamical conduction studies of the molecule with and without functional groups support the findings of single-molecule conduction experiments, and contradict the observations of molecular conduction in self-assembled monolayers. The ambivalent role of π conjugation in the operation of molecular circuits is highlighted.

Time-dependent Studies on Charge Transport using Local Atomic Orbitals as Basis

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We are developing a non-adiabatic time-dependent ab-initio simulation method PLATO using local atomic orbitals as the basis set. It is able to carry out either the self-consistent calculations based on Kohn-Sham equations or the computationally much cheaper tight-binding calculations. Ehrenfest approximation is used for the time propagation [1], and it is implemented by an efficient integrator.

Our aim is to use the time-dependent density functional theory as an alternative method to study the charge transport in nano-scale electronic devices. Preliminary studies on a ferrocene based system is carried out using the well known VASP code; and its transport properties are calculated using the standard Non-Equilibrium Green's Function methods [2, 3]. Results from these studies will be used to compare with those calculated from PLATO.

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Optimization of quantum Monte Carlo wave functions by energy minimization

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We present a simple, robust and highly efficient method for optimizing all parameters of many-body wave functions by energy minimization in quantum Monte Carlo calculations. Using a strong zero-variance principle, the optimal parameters are determined by diagonalizing the Hamiltonian matrix in the space spanned by the wave function and its derivatives [1-2]. We discuss the connection with previously-proposed energy minimization methods, namely the modified Newton method [3] and the perturbative energy fluctuation potential method [4]. Application of the method to electronic atomic and molecular systems show that it systematically reduces the diffusion Monte Carlo fixed-node error.

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Adsorption of alkali metals on graphite from Density Functional Theory Calculations

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We use density functional theory calculations to study the adsorption mechanism of lithium, sodium and potassium atoms on a graphitic substrate. The calculations were performed using plane waves basis, and the electron-core interactions are described using pseudopotentials. The influence of different parameters defining the calculation model, *v.gr.* the use of different exchange correlation kernels, the number of layers in the substrate and the number of special points sampling the Brillouin zone is analized in detail. These considerations bring light to the significant dispersion of results concerning the Li/graphite bond reported in the literature. Further analysis of the charge densities and difference charge densities shows that it is possible to understand the differences between the three studied systems, and in particular the ordering of the binding energies, through the interplay between electronic charge transfer and the properties of the associated cation/aromatic-ring complexes.

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Ab initio studies of magnetism induced by vacancies in graphene: influence of adsorbed species

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Magnetic carbon has aroused a lot of interest in the last years, due to the underlying new basic physics, and the appaling range of possible applications of magnetism in these materials, which makes the understanding of its origins and stabilization mechanisms of extreme importance. Motivated by experimental results previously published by one of the present authors [1], *ab initio* calculations have been performed using the program SIESTA, in the framework of Density Functional Theory (DFT), using norm-conserving PBE-GGA pseudopotentials, spin polarization and a DZP basis set. Studies on 12x12x1 supercells (287 atoms) have been performed to assess magnetic moments induced by graphene with a single carbon atom vacancy (SAV-g) and the effects of adsorption of foreign species on the system. For SAV-g we find a magnetic moment of $\approx 1.2\ \mu_B$, and the appearance of a narrow peak on the DOS at the Fermi energy (E_F). Atoms rearrange to form a pentagonal structure, opposite to which is located the magnetic center, on an atom with a dangling bond. While H/N adsorption onto the magnetic center induces quenching of the liquid spin on SAV-g, O causes it to completely vanish, all of these elements inducing a finite DOS at E_F. Allowing for relaxation of cell vectors changes the results dramatically: a deviation from the original symmetry of a perfect cell is seen on both cell vectors and angles. Moreover, the magnetism of H-SAV-g completely disappears, while N-SAV-g displays the same magnetic moment as for the unrelaxed cell. This suggests that the effect of mechanical tension is important for the magnetism in this system.

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The GW space-time formalism at finite temperatures

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We present the generalization of the space-time formulation of the GW approximation in many-body perturbation theory. The main changes are introduced in the treatment of the imaginary time and frequency dependency of the polarizability, screening, and self-energy. The discrete Matsubara frequencies and finite imaginary time intervals for integration are taken into account. Efficient fitting and interpolation schemes are developed to avoid a large increase in the grid sizes when going to metallic and finite-T systems.

Density functional calculations of titania nanosheets

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Titanium dioxide is an interesting material for a wide range of applications. The most stable polymorph is rutile, but anatase is commonly found in nanocrystalline samples. However, the structure of very small TiO_2 particles is difficult to be characterized experimentally. Ultrathin TiO_2 sheets ("nanosheets") give the unique possibility of studying nanosized titania systems both theoretically and experimentally (they can be prepared as supported films). We are performing a systematic study of the properties of TiO_2 ultrathin films obtained from anatase. We find that (001)- and (101)-oriented anatase nanosheets both give rise to particularly stable systems, though their structural features are very different. In the (001) case, the structure spontaneously relax to a lepidocrocite structure [1], where all the Ti atoms increase their coordination number from 5 to 6. In the case of (101)-derived films, the optimized structure is unprecedented: all the Ti atoms turn to 5-coordinated, and most O atoms are found 2-coordinated, giving rise to local coordination polyhedra similar to that characterizing the V_2O_5 structure. Both the TiO_2 films can be obtained as Pt-supported nanosheets: the lepidocrocite-type give rise to single-domain layers on Pt(110) [2], whereas the other one is formed on Pt(111) [3].

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Photoabsorption of Nanographene by Time-Dependent Density Functional Theory

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We have investigated photoabsorption spectra of triangular graphitic flakes (TGF) and graphitic ribbons (GR) with and without hydrogen termination by time-dependent density-functional theory calculations within a real-time scheme, focusing the effects of edge structures[1] and spin polarization on photoabsorption spectra. Major peaks in the low energy region of the spectra are attributed to the $\pi - \pi^*$ electronic transitions. The peak of strength function appears at $\sim$ 3 eV owing to $\pi - \pi^*$ transitions via edge states for a TGF with hydrogen (H) termination and at $\sim$ 6 eV owing to $\pi - \pi^*$ transitions at the Γ point for GR with H termination. Small structures in the strength function emerge at $0 \sim 2$ eV for either nanographenes after extractiong H atoms are found to originate from the electronic transitions between dangling-bond states. Spin polarization effect of a graphitic ribbon with Fujita-edge and Klein edge has been also found in the photoabsorption spectra. Thus, the present study indicates that the electronic states unique to nanographene can be captured in the optical absorption spectra.

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Hydrogen Bonding in Minerals

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The presence of hydrogen-bonds within the crystal structures of both hydrous and nominally anhydrous minerals has a marked effect on the physical properties of these materials. In this poster, we present the results of two recent density functional theory studies into this interesting class of materials.

In the first study, we have calculated the Γ-point phonon frequencies for a variety of hydrogen-bonded materials using density functional perturbation theory, at both ambient and high pressures. As this method provides us with accurate values for the hydrogen positions, it is therefore possible to examine the empirical relationships between both the $H\cdots O$ and O-H bond-lengths and the hydrogen stretching frequency, as previously determined by Novak [1974] and Libowitzky [1999] from experimental results.

The second study provides a significantly-improved model for the light hydrogen nuclei, treating them as delocalized quantum mechanical entities using path-integral molecular dynamics. Of course, this extra complexity comes at a tremendously-increased computational cost, and thus our study is limited to a single (high-symmetry) mineral: brucite, $Mg(OH)_2$. Our latest results will be presented.

Elastic properties of ZnO

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Elastic properties of ZnO polymorphs: wurzite-, zinc-blende-, rocksalt-structures, and yet experimentally undiscovered CsCl-structure were computed using the first principles plane-wave pseudopotential method in the scheme of density functional theory. Computed data was fitted to different parametrizations of the equation of state in order to obtain equilibrium volume and bulk modulus. The elastic behavior and the stability of the structures were investigated and compared to experimental data, where available. For each structure, electronic properties such as band structure and density of states were calculated within the LDA+U approximation.

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First-principles study of band alignments for β-Ge_3N_4 /Ge interface

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Recently, Ge and its alloy with Si have attracted great interest in high performance complementary metal-oxide semiconductor (CMOS) research because of higher intrinsic carrier mobilities [1,2]. The main impediment for Ge to replace Si is that its oxide is not as stable as SiO_2 on Si. Germanium Nitride (Ge_3N_4) is a potential gate dielectric for Ge based FETs, and its band alignment with Ge is an interesting issue[3,4].

First-principles calculations based on density-functional theory and generalized gradient approximation have been used to investigate valence and conduction band alignments for β-Ge_3N_4 (001)/Ge (111). The PDOS shows that there are no interface states in the band gap. The calculated valence and conduction band offset is about 2.33 eV and 1.51 eV, respectively, which indicates that the barriers between β-Ge_3N_4 (001)/Ge (111) are large enough to minimize possible carrier injection from gate electrode into channel.

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Transport and Optical Properties of Metals through Wannier Interpolation

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We present an efficient first-principles approach for calculating Fermi surface averages and spectral properties of solids, and use it to compute the anomalous Hall conductivity and the magneto-optical absorption of iron.

The first step is to perform a conventional first-principles calculation on a uniform grid of k-points in the Brillouin zone. We then map the low-energy electronic structure onto a set of maximally-localized, partially occupied Wannier functions, and evaluate the matrix elements of the Hamiltonian and the other needed operators between the Wannier orbitals, thus setting up an "exact tight-binding model". In this compact representation the k-space quantities are evaluated inexpensively using a generalized Slater-Koster interpolation. Because of the strong localization of the Wannier orbitals in real space, the smoothness and accuracy of the k-space interpolation increases rapidly with the number of grid points used in the initial first-principles calculation. This allows one to perform k-space integrals with *ab-initio* accuracy and tight-binding cost. In the Wannier representation, band gradients, effective masses, and other k-derivatives needed for transport and optical coefficients can be evaluated analytically, producing numerically stable results even at band crossings and near weak avoided crossings.

Calculation of core-level properties in pseudopotential-based electronic structure methods

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At present, the vast majority of ab initio molecular dynamics implementations use pseudopotentials which eliminate core electrons from the problem and change the shape of valence wavefunctions. However, accurate calculations of certain physical properties, e. g. core contribution to Fermi contact hyperfine couplings and core-level photoemission spectra, require explicit description the excluded states. We show the possible ways to overcome the problem and compare the results with all-electron calculations [1, 2].

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First principles molecular dynamics study of radiation damage of graphite and carbon nanostructures

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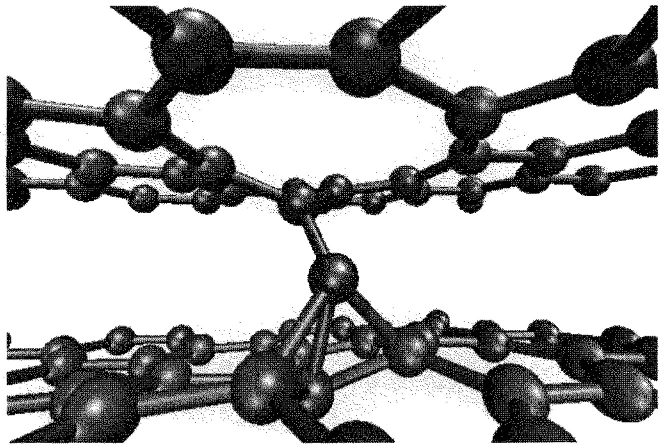
Understanding the mechanisms of radiation-induced defect formation in carbon materials is crucial in nuclear technology [1] and for the manufacturing of nanostructures with desired properties [2]. Using first principles molecular dynamics we perform a systematic study of the non-equilibrium processes of radiation damage in graphite on the picosecond timescale. Our study reveals a reach variety of defect structures (Frenkel pairs, in-plane topological defects) with formation energies of 5-15 eV. In addition, it clarifies the mechanisms underlying their creation and predicts unexpected preferences towards certain structures [3].



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Excitation energies of autofluorescent proteins in quantum Monte Carlo

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We present time-dependent density functional theory (TDDFT) and quantum Monte Carlo (QMC) calculations of the excitation energies of prototypical photoactive biomolecules and compare our results with other available correlated calculations and with experiments.

To access the performance of QMC in describing photoactive biosystems, we first study a simple chromophore model (pCA) of the Photoactive Yellow Protein (PYP) in vacuum and find excellent agreement with other available highly-correlated quantum chemical calculations. Our QMC excitations differ by as much as 0.8 eV from those computed within TDDFT.

We then focus on the excitation energies of the anionic form of the Green Fluorescent Protein (GFP) fluorophore. In particular, we investigate the dependence of the excitation energy on the size of the model chromophore and on the protein environment. We find that different theoretical approaches yield a large spread in excitation energies of small gas-phase models of the GFP chromophore; furthermore, these approaches support different physical pictures, in particular regarding the role played by the protein environment on the absorption spectra.

Ab initio calculations of structural and electronic properties of InAs having wurtzite crystal structure.

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The growth of new materials is a frequently occurring event in current semiconductor physics. The novelty of the fabricated systems demands a theoretical study of their structural and electronic properties, which will provide the necessary knowledge to exploit their features, corroborate the experimental analysis and design the materials of the future.

Motivated by the finding that InAs NanoWires (NWs) grow purely wurtzite, we focused our attention on the study of this new polymorph for which almost no previous calculations exist. We report our results on *ab initio* calculations of bulk InAs having wurtzite crystal structure.

All-electron LAPW calculations within the DFT/LDA approximation are used to obtain the structural properties. Within the same approximation, we have investigated the influence of relativistic effects on the electronic band structures.

LDA wrongly predicts InAs to be a zero-gap semiconductor, with the conduction band minimum (CBM) being at lower energy than the valence band maximum (VBM). Plane-wave pseudo-potential calculations were used to investigate the role played by the In 4*d* electrons in the "wrong band ordering" problem of the LDA bands of InAs.

The excited-state properties are investigated using methods based on many-body perturbation theory. To circumvent the "negative gap" problem, the quasiparticle band structure was calculated following a screened-exchange (SX) plus GW approach, finding good agreement with recent experimental results.

A scheme for the economical use of numerical basis sets in calculations with the SIESTA

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We demonstrate the effectiveness of an economical scheme that uses numerical basis sets in computations with the SIESTA. The demonstrated economical basis sets, in which high-level double-zeta basis plus polarization orbitals (DZP) are applied only for atoms of strong electronegativity and metal atoms while double-zeta basis (DZ) to the rest atoms of small proton-bound carboxylic acid clusters and Na-organic compounds, predict correct geometric structures very close to those obtained using DZP for all atoms. The use of economical basis sets can save about 30-50% of the CPU time that is used for calculations with large basis sets. This study provides a general guideline for basis set selection in SIESTA computations of large systems.

Surface chemical reactivity of amorphous silica in Quantum Mechanics / Molecular Mechanics simulations

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Quantum mechanics/molecular mechanics (QM/MM) approaches are currently used to describe several properties of silica-based systems, which are local in nature and require a quantum description of only a small number of atoms around the site of interest, e.g., local chemical reactivity or spectroscopic properties of point defects. We present a QM/MM scheme for silica suitable to be implemented in the general QM/MM framework recently developed for large scale molecular dynamics simulations, within the Quickstep approach for the description of the quantum region. Our scheme has been validated by computing the structural and dynamical properties of an oxygen vacancy in α-quartz, a prototypical defect in silica [1]. We have applied this scheme to the study of the grafting process of an organic molecule tetra-etoxy-silane (TEOS), on two-membered silicon ring at the surface of amorphous silica. This work aims at comparing the reactivity of two-membered ring and residual silanols (Si-OH bonds) for the grafting of a TEOS molecule which has the same functional group (ethoxy) of the organosilanes most used as silica-polymer coupling agents in the coatings of optical fibers. To study the grafting process we have made use of the metadynamics technique to deal with rare events within *ab-initio* molecular dynamics.

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C-doped AlN:
A ferromagnetic dilute magnetic semiconductor based on anions substitution

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We theoretically propose a new class of doping methods, anions substitution, for the recent hot research of II-VI/III-V DMSs. We have investigated ferromagnetism in C-doped AlN based on our new doping methods, and first-principles calculations based on the spin density functional theory are used. The doped anions are found spin polarized, and the system shows the ferromagnetic ground state while anion sites of AlN are substituted by 6.25% of C dopants. Additionally, we suggest that the codoping of Li can enhance the ferromagnetic stability of the system.

By first-principles calculations we have proposed a new type dilute magnetic semiconductor based on “anions” substitution rather than “cations” substitution of the host semiconductor. In AlN, single C at N site can be spin polarized with a magnetic moment of 1.0 μ, and the band structure is half metallic. At concentrations when C atoms couple to each other, ferromagnetism is energetically favored. Additionally, Li can be used to enhance the ferromagnetism of the system.

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