POSTER SESSION I

THURSDAY 10 JANUARY 2013

In alphabetical order of presenting author (underlined)

Electronic structure of Co doped ZnO from the GW perspective
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T3

The true role of many-body polarization forces in describing the properties of liquid water
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T5

Dispersion interactions in DFT and linear-scaling DFT
Lampros Andrinopoulos[1], Nicholas D. M. Hine[1], Arash A. Mostofi[1]
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T1

Theoretical studies on a gramicidin A channel using a linear-scaling DFT technique
M. Arita[1,2], M. Todorovic[3], W. Shinoda[4], D.R. Bowler[5] and T. Miyazaki[2,1]
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T6

Structure of liquid water from first-principles simulations with van der Waals interactions
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T5

Reaction pathways and structural properties by Quantum Monte Carlo
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T4

Electronic and Optical properties of ZnO Quantum Dots, Nanorods and Nanoflakes: an atomistic study
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FHI-aims becomes embedded: a full-potential QM/MM approach
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Are Polarization and Magnetization Really Bulk Properties?

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T9

Orbital density dependent functionals: a powerful tool for electronic structure calculations

Giovanni Borghi[1], Linh Nguyen[1], Andrea Ferretti[2], Cheol-Hwan Park[3], Nicolas Poilvert[4], Ismaila Dabo[5], Nicola Marzari[1]

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Range-separated approach to the RPA correlation applied to van der Waals bond and to diffusion of defects

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Variational approach to hydrogen's electronic structure

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Comparison of stress and total energy methods for the calculation of elastic properties of semiconductors

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Epinephrine geometrical parameters study using car-parrinello molecular dynamics

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Thermal conductivity and expansion of crystals from first principles

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T8

Wannier Functions study of chemical bonds in B12 and B28

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Defect Ordering in hard PbTiO3

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Protein field effect on the dark state of 11-cis Retinal in Rhodopsin by Quantum Monte Carlo

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T4

New implementations of the orbital minimization method in the SIESTA code

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T6

Study of the hydration effect on the carbamazepine geometric parameters using the Car-Parrinello molecular dynamic

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Adsorption of Small Molecules at Kaolinite: a van der Waals DFT study

Loic Roch[1], Stephen J. Cox[1] and Angelos Michaelides[1]

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Differential polarization effects with wave function/DFT embedding for excited states

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T6

Structure and Thermochemistry of Borosilicate Glass

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Second Order Møller-Plesset Perturbation Theory and Random Phase Approximation Correlation Energies with Resolution-of-Identity Approximation: An Efficient and Massively Parallel Gaussian and Plane Waves Approach

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Diffusion Monte Carlo for Heavy Atoms

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T4

A First Principles Approach to Thermal Transport in Nanomaterials

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Electronic transport properties of grain boundaries in graphene

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Exciton dispersion from first principles

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T3

Why is water difficult for DFT?
An analysis using GAP potentials and quantum Monte Carlo

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Implementation of the image charge method in QM/MM

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Efficient relativistic nuclear magnetic resonance J-coupling with pseudopotentials and the zeroth-order regular approximation

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First-principles calculation of Seebeck coefficient of $AgSbSe_2$

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T8

Study of Vanadium- and Cobalt-Benzene Half-Sandwich Arenes by Stochastic Quantum Sampling Approach

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T4

Performance of local orbital basis sets in the self-consistent Sternheimer method for dielectric screening of extended systems

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The GW approximation in GPAW

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Enhanced metallicity in armchair graphene nanoribbons with Cu impurities

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T8

Quasi-linear band structure and electronic transport in transparent conducting oxides

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Radiation damage in biological systems: Ab initio MD studies

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Electronic correlations and crystal structure distortions in BaBiO3

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Magnetic Spectroscopies with DFT + Hubbard (U,V)

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Infulence of exchane-correlation functional on local order competition in disordered phase of Ge2Sb2Te5: octahedral versus tetrahedral Ge

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Ab-initio Sternheimer-GW method for quasiparticle calculations

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Strongly-correlated quantum wires within Kohn-Sham Density Functional Theory

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Disorder effects in solid state systems beyond a single-site prospective: theories and applications

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Efficient evaluation of Fock exchange for non-localized wave-functions

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Polyamorphism in CO2 from ab initio molecular dynamics

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Z-method calculation of the Mg melt curve

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Structural and orbital phase transitions induced by Jahn-Teller distortions in KCuF3

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Extension of the SCE Formalism to Fractional Electron Numbers and Investigation of the Derivative Discontinuity

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Doping at the Si-SiO2 interface

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Topological surface state scattering in Antimony

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T8

Spin transport and magnetic behavior of boron nitride nanoribbons with magnetic impurities

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T8

Photoemission spectroscopy from Koopmans’ compliant functionals, and its application to the tautomeric populations of DNA and RNA nucleobases

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Spin state transition in LaCoO3: a DFT+DMFT aproach

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T4

Frequency-dependent Hubbard U corrections to DFT: A simple approach

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T3

Extending the random-phase approximation for electronic correlation energies: The renormalized adiabatic local density approximation

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Wavelets and Projector Augmented-Wave approach: an adaptive basis set for large-scale calculations at all-electron accuracy

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A new field-theoretic approach to linear scaling ab-initio molecular dynamics

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Optical Absorption in B−19 Cluster : A Time Dependent Density Functional Approach

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T2

Recent progress in the theory of flexoelectric response

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T9

Strong Isotope effect in phase II of Dense Solid Hydrogen and Deuterium

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T5

Computer simulation of the reaction mechanism of matrix metaloprotease MMP3 by QM/MM methods

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T6

Towards Petascale DFT-calculations: a new parallelization approach for linear response and exact exchange

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Kohn-Sham orbitals from Quantum Monte Carlo Density

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T4

Ab initio angle- and energy-resolved photoelectron spectroscopy with time-dependent density-functional theory

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Effective Hamiltonians for large-scale ab-initio lattice dynamics simulations of perovskites and related materials

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T6

Calculation of thermoelectric properties from first-principles

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T8

Optimized Structure and Vibrational Properties by Error Affected Potential Energy Surfaces

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Electronic structure of Co doped ZnO from the GW perspective

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Single shot GW (G0W0) and self consistent GW (scGW) quasiparticle density of states with different starting points include in GGA, GGA+U and HSE03 for Co doped zinc oxide are investigated. The gap energy is calculated nearer to experimental reports with G4W4 approximation and the effects of self-consistency in G and W are discussed. This correction is attributed to reduction of p-d repulsion and hybridization. The wurtzite crystal field split minority 3d-Co states to e and t_2 which the location of them is in doubt, especially with LDA and GGA calculation. In consideration to new many body scenario (GW) and its reputation to predict E_g and d binding energy in wide band semiconductor such as ZnO, ZnS and LiF, we have predicted the position of t_2 1.4-3.5 eV above the conduction band minimum i.e. it is impossible to predict the presence of ferromagnetism in the absence of defects in zinc oxide doped with cobalt even in sufficiently large n doping.

The true role of many-body polarization forces in describing the properties of liquid water.

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Although many water models have been designed, none is able to accurately predict most of the properties of water at different temperatures and pressures, particularly the so-called anomalous properties of water. It is important to identify the reasons why the accuracy of these models has been limited. To this end, we start with a highly-accurate pairwise interaction model and perform molecular dynamics simulations to predict the properties of liquid water at different temperatures. This pairwise model accurately predicts the experimental spectra of the water dimer. We then add many-body polarization forces, as represented by the Drude model, and repeat the simulations. Compared with the previous simulations, the properties of liquid water are in better agreement with experimental data, thus, clearly showing the influence of many-body polarization forces. From *ab initio* calculations, we estimate that the polarization forces account for only about half of the many-body forces in liquid water, the rest being made up of many-body exchange forces. We suspect that the inclusion of these non-pairwise additive exchange forces will lead to better agreement of our calculated properties with the experimentally determined values.

Dispersion interactions in DFT and linear-scaling DFT

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Semilocal functionals in Density Functional Theory (DFT) achieve high accuracy simulating a wide range of systems, but miss the effect of dispersion (vdW) interactions, important in weakly bound systems. We study two different methods to include vdW in DFT: First, we investigate a recent approach [1] to evaluate the vdW contribution to the total energy using maximally-localized Wannier functions. Using a set of simple dimers, we show that it has a number of shortcomings that hamper its predictive power; we then develop and implement a series of improvements [2] and obtain binding energies and equilibrium geometries in closer agreement to quantum-chemical coupled-cluster calculations. Second, we implement the vdW-DF functional [3], using Soler's method [4], within ONETEP [5], a linear-scaling DFT code, and apply it to a range of systems. This method within a linear-scaling DFT code allows the simulation of weakly bound systems of larger scale, such as organic/inorganic interfaces, biological systems and implicit solvation models.

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Theoretical studies on a gramicidin A channel using a linear-scaling DFT technique

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Gramicidin A (gA) system is known as an ion channel, which only allows monovalent cations to permeate. The structure of gA molecule is small and simple, and the gA ion channel is important as a model membrane protein. The system has been well studied both experimentally and theoretically, and gA is the only ion channel whose atomic resolution structures were available in 1990s. In the theoretical studies of this system, classical molecular dynamics simulations have been mainly used so far, but this approach is reported to yield a large energy barrier at the channel centre, which is not in accord with experimental results. There are also other reports showing such problems of the empirical force field and it is thus important to investigate this system with the first-principles approach.

In this talk, we will report our recent study on gA systems using our linear-scaling DFT code CONQUEST (*C*oncurrent *O(N)* *QU*antum *E*lectric *S*imulation *T*echnique). The code is efficient on parallel computers and we will show that it is now feasible to carry out stable *ab-initio* calculations on such a huge and complex system. In this work, we first studied the isolated gA system to clarify the accuracy of our *O(N)* DFT method and to achieve the reliable calculation conditions. Some basic information, such as the effects of side chains on the atomic and electronic structures was also examined. Then, we have recently employed large-scale DFT calculations on gA channel embedded in lipid bilayers. The systems (Fig.1) we have calculated consist of gA, DMPCs for lipid bilayers, water and some ions, including more than 15,000 atoms. We will demonstrate that SCF calculations are robust and efficient even for such large and complex systems. We have calculated the atomic forces and compared them with those obtained by the classical force field, CHARMM36, and will report whether the CHARMM force field shows a good performance in this system. In particular, we will focus on the differences for the atoms near monovalent or divalent cations. The effects of the vdW interactions computed by the DFT-D scheme will be also discussed.

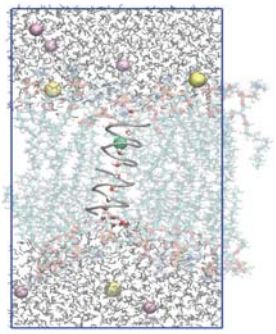
Figure 1: gA system

Structure of liquid water from first-principles simulations with van der Waals interactions

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Ab initio molecular dynamics (AIMD) simulations of water using density functional theory (DFT) with semi-local (GGA) exchange-correlation functionals have been shown to be fairly inaccurate when comparing with experimental results for the structural and diffusive properties of the liquid. Using the SIESTA [1] DFT method we present an AIMD study of liquid water using three different non-local functionals that aim to provide a description of van der Waals (vdW) interactions, missing in conventional GGA functionals. For our calculations we employ simulation boxes of up to 200 molecules and MD runs of 20 ps. We discuss the effect of vdW interactions on the equilibrium density and compressibility of liquid water at ambient conditions, the structural information given by the radial distribution function for a range of densities, and the diffusivity, showing an overall improvement with respect to GGA [2]; in particular, the equilibrium density is noticeably improved, and the diffusivity is reproduced in good agreement with experiment without the need for temperature rescaling [3]. Finally, the large system sizes used allow us to investigate for the first time from *ab initio* simulation the possibility of extended structural fluctuations, of noticeable interest due to the suggestion of a high/low-density split in the liquid [4]; our results from a local density analysis show evidence of clusters of ∼25 molecules.

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Reaction pathways and structural properties by Quantum Monte Carlo

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Quantum Monte Carlo methods have been used to investigate the intramolecular reaction pathways of the simplest conjugated diene, i.e. the *s-trans*-1,3-butadiene[1]. The ground state geometries of the three conformers *s-trans*, *s-cis* and *gauche*, as well as the cyclobutene structure have been fully optimized at the Variational Monte Carlo (VMC) level, obtaining an excellent agreement with the experimental results and other quantum chemistry high level calculations. Transition state geometries have been also estimated at the VMC level for *s-trans* to *gauche* torsion barrier of 1,3-butadiene and for the conrotatory ring-opening of cyclobutene to the *gauche*-1,3-butadiene conformer. The energies of the conformers and the reaction barriers were calculated at both the VMC and the Lattice Regularized Diffusional Monte Carlo (LRDMC) levels, providing a precise picture of the potential energy surface of 1,3-butadiene and supporting one of the two model profiles recently obtained by Raman spectroscopy [Boopalachandran *et al.*, *J. Phys. Chem. A* **115**, 8920 (2011)].
We have also calculated the convergence of the Bond Length Alternation (BLA) for polyacetylene chains, defined as the difference between the central double and single carbon bonds of the chains, as the function of the number of monomer units that define them. We have obtained results in the range of the available experimental x-ray data that predicts a BLA of 0.09 Å.

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Main Topic: T11 Other methods

Electronic and Optical properties of ZnO Quantum Dots, Nanorods and Nanoflakes: an atomistic study

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In the present work we study the electronic and optical properties of ZnO quantum dots, nanorods and nanoflakes using atomistic empirical pseudopotentials [2,3] with the relaxed atomic positions [4] and configuration interaction for the excitonic states [5]. This suggests the possibility to tailor the optical polarization by a change in morphology. We elucidate the underlying mechanism from an analysis of the valence band structure and highlight the importance of exciton correlations.

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

Theory and Methods:
T3 Many-Body Techniques for Real Materials
T11 Other methods

Applications:
A1 Nanoscience

FHI-aims becomes embedded: a full-potential QM/MM approach

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Nanostructured oxide surfaces promise a wide range of applications in surface chemistry and catalysis. Exploring the zoo of combinatorial compound material for the ultimate candidate for a certain application may best be tackled by computational studies. When addressing those functionalities through quantitative first-principles calculations, applying periodic boundary conditions (PBC) becomes numerically inefficient or even unfeasible at a certain system size, especially when going beyond the semi-local DFT level of theory. Exploiting the localized character of those systems we develop a highly efficient embedding setup to overcome limitations through system size. In this setup the nanostructure and immediate oxide surrounding is described quantum mechanically, while the long-range electrostatic interactions with the support are accounted for through a monopole field. A transition shell between both regions is introduced to prevent electron leakage into the Coulomb singularities and wrong chemical behavior through the creation of dangling bonds at the boundary of the quantum mechanical (QM) zone. In this transition shell oxide particles are represented through norm-conserving pseudopotentials [1] in the fully separable Kleinman-Bylander form [2]. We report details of the implementation of this scheme into the FHI-aims package [3]. For the optimization of the model parameters (size of QM-region, thickness of connecting shell) we reference against supercell geometry data, exploiting the FHI-aims capability to treat finite cluster and PBC supercells within the same numerical framework. Not being restricted to PBC calculations, the developed set-up is ultimately also capable to efficiently deal with charged states, which will be a fundamental asset for the description of charge transfer processes e.g. in photoinduced catalysis.

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Are Polarization and Magnetization Really Bulk Properties?

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Geometrical and topological properties are generally expressed as Brillouin-zone integrals. But we observe that the $\mathbf{k}$-space is an artificial construct: all bulk properties must be embedded in the ground state density matrix $\rho(\mathbf{r}, \mathbf{r}')$, "nearsighted" in insulators, independently of the boundary conditions, either periodic (PBCs) or "open" (OBCs). In a recent paper [1] we have shown that the Chern invariant has indeed a real space expression in terms of ρ, and can be evaluated on a finite sample within OBCs.

Here we address the macroscopic polarization $\mathbf{P}$ and the (orbital) magnetization $\mathbf{M}$, essential ingredients of the in-medium Maxwell equations, which are also expressed as Brillouin-zone integrals. A basic tenet of the modern theory is that the bulk electron distribution determines $\mathbf{P}$ only modulo a "quantum": therefore $\mathbf{P}$ is not independent of the boundaries, and therefore is *not* a bulk property in the above sense. Instead $\mathbf{M}$ is not affected by any quantum indeterminacy and an expression for it in terms of the bulk ρ—independently of the boundaries—is not ruled out: we have explicitly found such expression. In a finite homogeneous sample, within OBCs, the macroscopic magnetization is unambiguously cast as a function of the bulk $\rho(\mathbf{r}, \mathbf{r}')$. Remarkably, our approach applies even to topological (Chern) insulators, where $\mathbf{M}$ explicitly depends on the chemical potential. The topologically protected boundary currents contribute to $\mathbf{M}$, but even their contribution is "bulk" in the above sense; the value of $\mathbf{M}$ is robust and cannot be altered by acting on the boundaries only. We stress that, instead, $\mathbf{P}$ can be varied (by a quantum) by acting on the boundaries only. As in Ref. [1], even here simulations performed on a 2d model Hamiltonian within OBCs demonstrate our approach.

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Orbital density dependent functionals: a powerful tool for electronic structure calculations.

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Orbital density dependent Non-Koopmans functionals are a powerful tool for extending conventional density functionals such as LDA and PBE to the description of quasiparticle optical properties. Removing the electron self-interaction bias through piecewise linearization of total energy with respect to fractional changes of particle number enables to correct the band-gap of semiconductors and insulator in a similar way as the Hubbard U correction to LDA does. Non-Koopmans functionals are universal functionals of the orbital densities apart from a single material dependent screening parameter, which can be calculated in an ab-initio fashion from a density functional calculation on the neutral and on the ionized system. Rather than on an orbital subset, as the LDA+U Hamiltonian, the Non-Koopmans correction acts on all valence and on a few conduction orbitals of the system, whose shape is optimized throughout the functional minimization. The outcome of a total energy calculation is a set localized wavefunctions, which may serve both as Wannier functions for downfolding procedures, and as basis sets for LDA+U or LDA+DMFT calculations, for which they can provide also a self-consistent definition of U. This poster provides a comprehensive introduction and overview of the capabilities of these orbital dependent functionals, shows their performance on benchmark molecular and extended systems, and discusses very important theoretical issues such as the necessity to allow for complex minimizing orbitals, and the possibility of lower total energy minima when relaxing their usual orthonormality constraint.

Range-separated approach to the RPA correlation applied to van der Waals bond and to diffusion of defects

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The Random Phase Approximation (RPA) is a promising approximation to the exchange-correlation energy of Density Functional Theory (DFT), since it contains the van der Waals (vdW) interaction and yields a potential with the correct band gap. However, its calculation is computationally very demanding. We apply a range separation concept to RPA and demonstrate how it drastically speeds up the calculations without loss of accuracy. The scheme is then succesfully applied to a layered system subjected to weak vdW attraction and to address the controversy of the self-diffusion in silicon. We calculate the formation and migration energies of self-interstitials and vacancies taking into account atomic relaxations. The obtained activation energies deviate significantly from the earlier calculations and challenge some of the experimental interpretations: the diffusion of vacancies and interstitials have almost the same activation energy.

Main Topic: T11 Other methods

VARIATIONAL APPROACH TO HYDROGEN'S ELECTRONIC STRUCTURE

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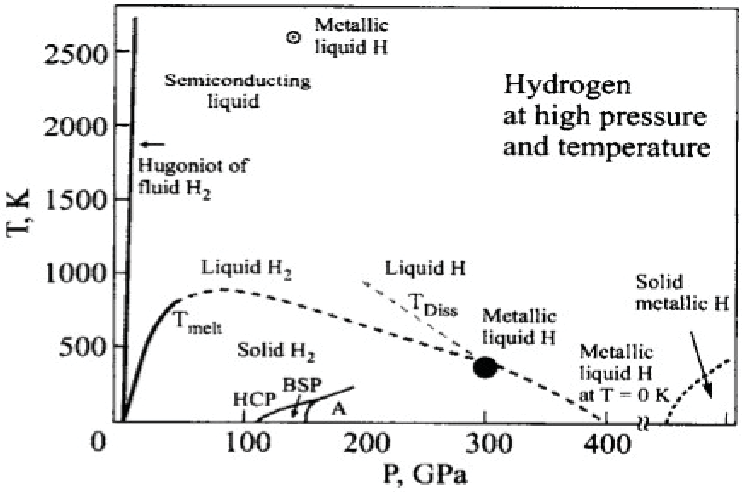
Hydrogen has a complex and still not well understood phase diagram, in particular at very high pressures and temperatures.



Computational studies of its phase diagram are convenient, since it is extremely difficult and often impossible to experimentally achieve such an high pressure and temperature. Being able to accurately describe the electronic structure is a key ingredient in this investigation.

The variational approach has the big advantage that it permits to control on the quality of the trial wavefunction used to describe the electronic structure, and it is therefore easy to compare different results (the function that gives a lower variational energy is to be favored). The product of the Slater Determinant given by the orbitals found from a mean field approach and a so-called Jastrow correlation function, that takes two-body correlations into account, has shown to give accurate results and to work well for different phases. Nevertheless, we have investigated also a different trial function, called Shadow Wave Function, that potentially gives an even larger flexibility and allows for even more accurate calculations.

Comparison of stress and total energy methods for the calculation of elastic properties of semiconductors

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Density functional theory (DFT) has proven to be a reliable frame for the calculation of elastic properties of semiconductors, providing reasonable agreement with experimental measurements. DFT is also a useful tool for the prediction of elastic constants of materials that are difficult to grow. These properties can be obtained either by calculating the total energy of the crystal as a function of strain or, equivalently, by calculating the stress as a function of strain. Since total energy and stress are related via a strain derivative, one would expect these two approaches to yield the same results. However, because of how the two methods are implemented in practice in the context of modern DFT codes, this is only the case if a very expensive calculation is carried out. Although these differences have already been noticed [1,2], there seems to be little general awareness on the issue. In particular, there is no conclusive comparative work on which method offers better results, in terms of convergence speed and consistency of coefficients obtained by straining the crystal in different ways. In this poster, we explore the calculation of the elastic properties of zinc-blende and wurtzite semiconductors using the two different approaches: stress and total energy as a function of strain. Differences are found in convergence rate between the two methods especially in low symmetry cases, where there is a much slower convergence for total energy calculations with respect to the number of plane waves and **k** points used. The stress method is also observed to be much more robust for the elastic constants calculated in different strain branches for the systems studied [3,4].

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EPINEPHRINE GEOMETRICAL PARAMETERS STUDY USING CAR-PARRINELLO MOLECULAR DYNAMICS

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Epinephrine or adrenaline is an monoamines belong to the group of the catecholamines. It acts as circulating hormone and neurotransmitter, regulating heart rate, blood vessel and air passage diameter. Epinephrine is water soluble and in the biological system at pH = 7.0, it has its amine group totally protonated, where the dominating conformational arrangement involve the secondary alcohol functional group as a hydrogen acceptor. The aim of the present work was to study the dynamics of the epinephrine geometrical parameter using the Car-Parrinello Molecular Dynamics. In order to study the effect of the protonation of epinephrine, two trajectories were simulated for 36 ps. Vanderbilt ultrasoft pseudopotentials were employed to represent core-valence electron interactions and a plane wave basis set was used to expand the valence electronic wave function with an energy cutoff of 25 Ry and 200 Ry cutoff was used for the expansion of the augmented charge density in the proximity of atoms. The electronic structure was treated within the generalized gradient approximation to density functional theory through the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The simulations showed that the protonation of amine group change some geometrical parameters of epinephrine and the results agree very well with experimental values from x-ray data.

Keywords: epineprine, Car-Parrinello molecular dynamic, geometric parameters

Thermal conductivity and expansion of crystals from first principles

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A number of interesting properties of crystals at non zero temperature are determined by ionic vibrations, such as the thermal expansion or the thermal conductivity. The typical approach in the description of vibrations is the harmonic approximation. However, at this very simple level of modeling, the harmonic approximation of phonons fails completely in the description of many finite temperature effects. For example the thermal conductivity of a harmonic crystal is infinite while the equilibrium volume doesn't change with the temperature. It is therefore necessary to overcome those difficulties by including anharmonic effects. By considering the dependency of vibrational frequencies on the volume within the theoretical framework of the Quasi-harmonic approximation, we study the thermal properties of a single layer of MoS_2. In particular, we present the Grueneisen parameters and the thermal expansion. We find that the presence of a negative Grueneisen parameter for the out-of-plane ZA mode does not suffice to let the layer contract at non-zero temperatures, as it is instead observed in other layered systems such as graphene. Therefore the thermal expansion is non-negative at any temperature. The anharmonicity arising from the lowest order phonon-phonon scattering allows us to compute the thermal conductivity by solving the Phonon Boltzmann. We apply it to the case of bulk silicon and germanium, where we point out the effect of alloying and of boundary scattering, and we apply it to the case of graphene, where strain and boundary scattering strongly affect the thermal conductivity of the system. In the poster we briefly describe the theoretical framework used and present the results for the studied systems. All ab-initio data are computed with the open source software Quantum Espresso (Giannozzi et al., Phys.: Condens. Matter 21, 395502 (2009)).

Wannier Functions study of chemical bonds in B_{12} and B_{28}

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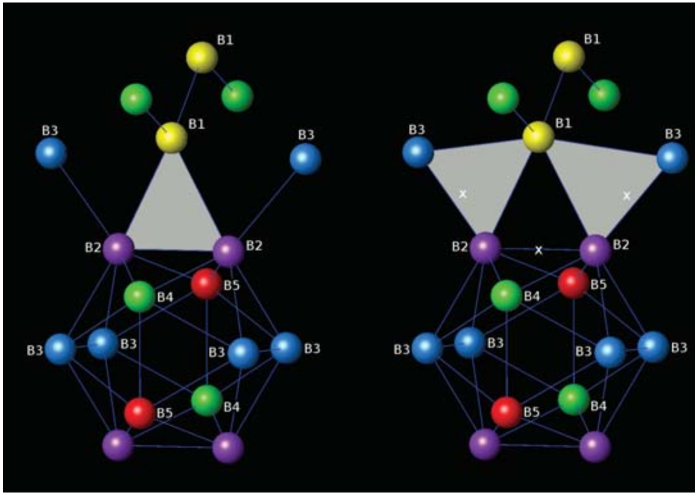
We report a study of the chemical bond network in two Boron polymorphs (B_{12} and the recently discovered high-pressure phase B_{28} [1]) by Maximally Localized Wannier Functions (MLWFs) [2]. Starting with the B_{12} phase, whose bonding network is well understood, we have found three *two-center* (2c) MLWFs and two *three-center* (3c) MLWFs connecting neighboring boron icosahedra, in addition to 13 *skeletal* MLWFs, in agreement with Bader's topological analysis.

The situation is different in B_{28}, whose structure is composed by a network of B_{12} icosahedra linked by B_2 dumbbells. There Bader's analysis found a 3c bond between B1 and B2 atoms (see figure, left panel) and no evidence of bonding between B1 and B3 atoms. The MLWFs revealed instead a pair 3c bonds (between B1, B2 and B3 atoms), whose center, however, is shifted towards the B2-B3 bond (see figure, right panel). By carefully analyzing the MLWFs of the icosahedra, we have found that the B2-B2 Wannier Function has a substantial multi-center character, extending not only on the two edge-sharing faces of the icosahedron, but also towards the B2-B1-B2 triangle.



Finally, we analyzed the electronic structure of the two polymorphs, by constructing and diagonalizing the minimal tight-binding Hamiltonian in the Wannier basis.

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Defect Ordering in hard $PbTiO_3$

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Hardening and softening of ferroelectric materials can be engineered through the addition of dopants, and is a key technique to tailor dielectric and piezoelectric properties. Hardening is typically driven by the addition of acceptor dopants, and leads to small electromechanical coefficients and pinched hysteresis loops. Softening can be induced by the addition of donor dopants, which leads to large electromechanical coefficients and open hysteresis loops. Doping results in the formation of defects which interact with the domain walls present in the material. We use here first-principles calculations to show how acceptor dopants lead to the formation of defect complexes which align with the polarization axis and stabilize the ferroelectric domains. This defect ordering is consistent with aging phenomena in hard PZT, where hard properties are developed over a period of time. Calculation on donor dopants do not show a driving force towards ordering, consistent with the macroscopic evidence of a lack of aging. In addition, we corroborate the AC and DC conductivity data obtained in acceptor-doped materials with first-principles activation energies for oxygen vacancies' hopping, calculated through nudged elastic-band calculations. Last, we suggest that undoped materials can develop hard properties through ordering of the lead-oxygen divacancies, and the energy profile for these long-range interactions is investigated.

Protein field effect on the dark state of 11-*cis* Retinal in Rhodopsin by Quantum Monte Carlo

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The accurate determination of the geometrical details of the dark state of 11-*cis* Retinal in Rhodopsin represents a fundamental step for the rationalization of the protein role in the optical spectral tuning in the vision mechanism [1].
We have calculated high level geometries in gas phase and in protein environment using the correlated Variational Monte Carlo method [2]. The Bond Length Alternation of the conjugated carbon chain of the chromophore in gas phase shows a significant reduction when moving from the β-ionone ring to the nitrogen whereas, as expected, the protein environment reduces the electronic conjugation.
The proposed dark state structure is fully compatible with solid-state NMR data reported by Carravetta *et. al.* [*J. Am. Chem. Soc.*, 126:3948, 2004]. TDDFT/B3LYP calculations on such geometries show a blue opsin shift of 0.28 and 0.24 eV induced by the protein for S_1 and S_2 states, consistently with literature spectroscopic data [3].

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New implementations of the orbital minimization method in the SIESTA code

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The orbital minimization method (OMM) is the name given to a class of iterative algorithms devised for solving the generalized eigenvalue problem in the context of linear-scaling density-functional theory (DFT). The central idea of the method is to find the Wannier functions that describe the occupied subspace by direct unconstrained minimization of an appropriately constructed functional [1,2]. We report on several new implementations of the OMM in the SIESTA [3] DFT code. Firstly, we demonstrate its potential as a conventional cubic-scaling DFT solver, since the well-known problem of local minima present in the linear-scaling implementation disappears when the Wannier functions are allowed to extend over the whole system. The resulting algorithm is efficient due to the fact that no explicit orthogonalization is required between orbitals, and that the solution from each minimization can be reused iteratively for multiple self-consistent field steps and *ab initio* MD steps; we show that this method is competitive with explicit diagonalization even for atomic orbital codes, despite the large ratio of occupied states to total basis size. Secondly, we discuss two approaches for imposing the correct electron number in the augmented OMM of Kim *et al.* [4] that can be used with Wannier localization for linear-scaling calculations: an automated adjustment of the chemical potential, and a projected gradient method.

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Study of the hydration effect on the carbamazepine geometric parameters using the Car-Parrinello molecular dynamic

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The carbamazepine (cbz) is a medicine specially used in the treatment of epilepsy, bipolar disorder and trigeminal neuralgia. It is also indicated in the treatment of attention-deficit hyperactivity disorder, schizophrenia, phantom limb syndrome, complex regional pain syndrome, paroxysmal extreme pain disorder and post-traumatic stress disorder. In the present work, the Car-Parrinello Molecular Dynamics using plane waves and Vanderbuilt ultrasoft pseudopotentials was used to study the hydration effects on the cbz geometric parameters in the NVT ensemble at 300 K. For this intent, two trajectories of 30 ps were built: first one for the isolated cbz and the second for the cbz in aqueous solution.

The geometric parameters for the benzene and pyridine rings from isolated cbz, solvated cbz and x-ray data are very similar, i.e., the solvation process does not affect these rings, showing its hydrophobic character. However, the geometric parameters for carbamoyl group are largely affected by aqueous solvation process. These changes are attributed to the strong hydrogen bonds formation between the water molecules and the atoms comprised in the carbamoyl. The mean residence time and radial distribution functions of water molecules in the solvation spheres centered on oxygen, nitrogen and hydrogen atoms from carbamoyl group show that these hydrogen bonds are very stables.

From this work, we conclude that the aqueous solvent modify only the geometric parameters of the cbz carbomoyl group and the aqueous solvation does not affect the geometric parameters of benzene and pyridine rings, showing the strong hydrophobic character of this rings. In addition, we observe that the hydrogen bonds between carbomoyl group and the water molecules are strong and stable.

Adsorption of Small Molecules at Kaolinite: a van der Waals DFT study

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Clay minerals are a major component of the solid material in the Earth's crust, whose uses have been known since ancient times. Even today, clay minerals are still used in ceramics and are important in a wide range of fields such as medicine, adhesives, paints, oil drilling, radioactive waste and molecular sieves [1,2]. Clay minerals also have a significant environmental impact as they can help cleanse soils and groundwater through absorption of pollutants, and they also act as catalysts to ice nucleation in the upper troposphere. Having a theoretical understanding of how molecules adsorb at the surfaces of these minerals may therefore lead to improved ways to control such processes.

In this poster, we present results where we compare the performance of standard GGA functionals with the recently developed vdW-DF methods [3–5]. We show that although accounting for dispersion interactions does not drastically alter the adsorption structures, the relative stabilisation due to van der Waals interactions is system dependent. Even for small molecules, inclusion of dispersion interactions can be enough to change the relative stability of different adsorbate species. This highlights the need the properly account for dispersion interactions when modelling environmentally relevant processes, such as groundwater decontamination.

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Differential polarization effects with wave function/DFT embedding for excited states

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Embedding potentials are frequently used to describe the effect of an environment on the electronic structure of molecules in larger systems, including their excited states. If such excitations are accompanied by significant rearrangements in the electron density of the embedded molecule, large differential polarization effects can take place, and state-specific embedding potentials are required for an accurate theoretical description. We show that simple strategies to include environmental effects in terms of effective one-electron operators break down if state-specific embedding potentials are used, and propose a simple correction that leads to significantly improved excitation energies.

We demonstrate these concepts within a wave function/density functional theory (WF/DFT) hybrid scheme, where the active subsystem is described by multireference perturbation theory (CASPT2) or quantum Monte Carlo (QMC) methods. The effect of the environment is included via density-based state-specific embedding potentials obtained with the aid of orbital-free DFT. We illustrate the good performance of our embedding scheme in describing the excitations of a set of small molecules in various solvents.

Main Topic: T5 Ab-initio Molecular Dynamics

Structure and Thermochemistry of Borosilicate Glass

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We study the ternary B_2O_3-SiO_2 glass system using density functional calculations to accurately access the enthalpy of formation of amorphous and (hypothetical) crystalline structures. While studied since more than 100 years, the B_2O_3-SiO_2 system has not revealed another crystal phase besides the two antipodes, boria and silica.

Using the melt-quench approach and standard ab-initio molecular dynamic simulations we generate over 100 models of a-SiBO of different composition. All structures exhibit trigonal planar BO_3 units and tetrahedral SiO_4 units, and thus appear to be mixtures of amorphous a-B_2O_3 and a-SiO_2. Using the computed enthalpies of formation of a-B_2O_3, a-SiO_2, and mixed a-SiBO models, we find that the enthalpy of mixing of a-SiBO resembles closely the available experimental data. However, around a composition corresponding to 33 mol% of B_2O_3, we compute a negative enthalpy of formation, indicating a highly favorable conformation in borosilicate glass.

To investigate this trend further, we employed an ab-initio random structure search to find crystalline structures of $Si_2B_2O_7$. Generating of over 1000 models provided at least two candidate crystal structures, for which the enthalpy of formation with respect to the crystal structures of D-boria and D-quartz is comparable with 0 eV.

Hence, we find strong indication for a very favorable composition of borosilicate glasses and propose that it might be feasible to crystallize the first ternary SiBO compound for the composition $Si_2B_2O_7$.

Second Order Møller-Plesset Perturbation Theory and Random Phase Approximation Correlation Energies with Resolution-of-Identity Approximation: An Efficient and Massively Parallel Gaussian and Plane Waves Approach

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The canonical second-order Møller-Plesset perturbation energy (MP2) and the Random Phase Approximation (RPA) correlation energy, are increasingly popular post-Kohn-Sham correlation methods. Here a novel algorithm, based on a hybrid Gaussian and Plane Waves (GPW) approach with the resolution-of-identity approximation (RI), is developed for MP2 and RPA correlation energies of finite and extended system. The key aspect of the method is that the three center electron repulsion integrals $(\mu\nu|K)$ necessary in the RI approximation are computed by direct integration between the products of Gaussian basis functions $\mu\nu$ and the electrostatic potential arising from the RI fitting densities K. The electrostatic potential is obtained in a plane waves basis set after solving the Poisson equation in Fourier space. In particular for condensed phase systems, this scheme is highly efficient. The RI approximation allows to speed up the MP2 energy calculations by a factor ~ 10 compared to the canonical implementation, but still requiring $O(N^5)$ operations. On the other hand, in the RPA case, the combination of RI and imaginary frequency integration reduces the computational effort from $O(N^6)$ to $O(N^4 \log N)$. Furthermore, our implementation has low memory requirements and displays excellent parallel scalability up to tens thousands of processes. In this way, RI-MP2 and RI-RPA calculations for condensed phase systems containing hundreds of atoms can be performed within minutes.

Diffusion Monte Carlo for Heavy Atoms

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Diffusion Monte Carlo (DMC) is one the most accurate methods for calculating properties of molecules and periodic systems. In standard formulation, DMC is non-relativistic method, but it can also handle heavier atoms, where only scalar relativistic effects are present, with use of effective core potentials. But it can not provide description of systems dominated by spin-orbit coupling effects in heavy atoms. In this work, we propose an extension to DMC algorithm to treat also spin-orbit coupling. In this case, total spin of the system is not fixed, and we define new continuous representation of spin variable. Further we modify projection operator to obtain ground state of Hamiltonian (excited states are also possible with proper modification). Inclusion of spin-orbit interaction is done by using fully relativistic pseudopotentials. We demonstrate partial results on model systems.

A First Principles Approach to Thermal Transport in Nanomaterials

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A predictive theory for evaluating thermal conductivity is essential for the design of new materials for efficient thermoelectric refrigeration and power generation [1]. The development of a predictive quantum-mechanical theory requires an accurate microscopic description of the harmonic and anharmonic interatomic forces and the exact solution of the Boltzmann Transport Equation (BTE). In this contest ab-initio techniques have been used only recently for studying thermal transport in silicon, germanium and diamond [2–4]. When heat is mostly carried by lattice vibrations a correct theoretical prediction of thermal transport properties cannot leave aside an accurate description of the phonon-phonon interactions and lifetimes. These quantities are related to second and third order derivatives of the ground state energy with respect to atomic displacements. Specifically second order interatomic force constants determine phonon frequencies, group velocities and phonon populations while third order force constants determine anharmonic phonon scattering rates and line widths. Third order derivatives can be computed fully ab-initio using the 2n+1 theorem in the framework of Density Functional Theory. An efficient implementation of this method already exists for zone-centered modes [5], but until now a general implementation was lacking and fully first principle calculations of thermal transport had always required the use of extremely computing expensive super-cells. We recently filled this gap by developing a general implementation of the 2n+1 theorem in the Quantum-ESPRESSO package [6]. We are now able to evaluate the anharmonic coupling coefficients for any wave-vectors triplets without the need of super-cells. The harmonic and anharmonicinter-atomic force constants are then used as only inputs for obtaining the exact solution of the Boltzmann transport equation. In this talk a first-principles theoretical approach to calculate the lattice thermal conductivity of graphene, graphite and diamond based materials will be presented. I will show how for these systems is necessary to go beyond the single mode relaxation time approximation and to accurately describe the umklapp processes.

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Electronic transport properties of grain boundaries in graphene

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A number of recent experimental works reveal the polycrystalline morphology of graphene at micrometer length scales [1-3]. Dislocations and grain boundaries, the intrinsic topological defects in polycrystalline materials, are expected to strongly affect the electronic transport properties of graphene [4]. In my poster, I will talk about our systematic investigation of the ballistic transmission of charge carriers through the one-dimensional grain-boundary defects within the tight-binding model framework. The investigated grain boundaries are constructed to satisfy the conservation of coordination number of carbon atoms [5]. The relations between the structure of grain boundaries and their electronic transport properties will be discussed. Finally, the valley filtering capabilities of several grain boundaries are showed. This could represent one starting point for using the valley index degree of freedom of graphene charge carriers as ”quantum of information” in modern computing.

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Exciton dispersion from first principles

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The Bethe-Salpeter equation (BSE) is the state-of-the-art approach to calculate optical spectra of solids [1]. Indeed, it is a powerful tool that also provides a first-principles description of excitons. Here we present a generalization of the BSE implementation [2] that is able to deal with excitations (excitons and plasmons) with finite momentum transfer, as measured by electron energy loss (EELS) and Inelastic X ray (IXS) spectroscopies. We discuss the dispersion of bound excitons (both visible and dark) in prototypical materials, like wide-gap insulators (LiF and solid argon) and molecular solids (picene and pentacene) [3]. The analysis of the results allows us to disentangle the different contributions stemming from the electron-hole interaction and the electronic band dispersion, and to give an explanation of the exciton revival at large q measured by IXS in LiF [4].

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Why is water difficult for DFT?
An analysis using GAP potentials and quantum Monte Carlo

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Standard DFT methods have serious problems in describing water systems, including: inaccurate energetics of the water dimer in some cases; wrong energy ordering of isomers of the water hexamer; poor relative energies of different ice structures; gross errors in the equilibrium density of the liquid; liquid often over-structured and under-diffusive. The origins of these DFT errors have been hotly debated for many years. We show how Gaussian Approximation Potentials (GAPs) [1] and quantum Monte Carlo simulation [2,3] can be used to analyze where the DFT errors come from.

We separate the total energy of any water system into its 1-body, 2-body and beyond-2-body components, using the standard many-body expansion. GAP methods are used to create very accurate and rapidly computable representations of the errors of any chosen DFT relative to coupled-cluster benchmark energies for large samples (a few thousand configurations) of the water dimer. The GAP representations allow us to correct almost exactly for 1- and 2-body errors of any DFT functional for any type of water system. The remaining DFT errors are, by definition, beyond-2-body errors. Quantum Monte Carlo (QMC) gives very high accuracy for a variety of water systems, including clusters and ice structures. Using QMC energies as benchmarks, we use the GAP analysis to determine, for any water system, the amount of DFT error attributable to 1-, 2- and beyond-2-body energy. We illustrate how the analysis works for isomers of the water hexamer, ice structures, and nano-droplets in thermal equilibrium. We find that the distribution of DFT errors between many-body components depends strongly on the chosen functional.

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Implementation of the image charge method in QM/MM

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A method for including polarization effects within hybrid quantum mechanics/molecular mechanics (QM/MM) simulations of physisorbed adsorbate-metal systems is presented. In a standard QM/MM description, the adsorbed molecules are treated by QM and the metal by MM. The interactions between adsorbate and metal are usually described by a pair potential where electrostatic interactions are neglected. However, polar adsorbates can induce charges in the metal and interact with these charges. This classical phenomenon is referred to as image effect. It was shown that image charges are important for determining the assembling behavior of organic molecules on metal surfaces [1]. Image charges are also needed for a comprehensive description of processes at electrode interfaces [2].

In this work, the image charge method was implemented in the QM/MM module [3, 4] of the CP2K program package. The implementation is based on the Siepmann-Sprik scheme [5], where the image charge distribution in the metal is modeled by a set of Gaussian charges centered at the metal atoms. The image charges are determined self-consistently by imposing the constant-potential condition within the metal. The image charge method was applied to DNA bases and nitrobenzene at Au(111) interfaces and the results were compared to full DFT calculations.

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Efficient relativistic nuclear magnetic resonance J-coupling with pseudopotentials and the zeroth-order regular approximation

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Nuclear Mangnetic Resonance (NMR) is a widely used experimental technique in chemistry, biology and materials science. Recent experimental advances in solid-state NMR, such as higher field strengths and ultra-fast spinning speeds, have increased interest in the calculation of NMR parameters of extended systems in order to aid the interpretation and design of experiments. J-coupling is one such parameter and is the indirect magnetic coupling of two nuclear magnetic moments via bonding electrons, a highly sensitive measure of the local bonding environment of a nucleus. Recently [1] a plane-wave pseudopotential theory of J-coupling using Blöchl's projector augmented wave (PAW) [2] was developed. The approach has been successfully applied to systems containing light elements [3]. However, it is known that in order to describe J-coupling involving heavier elements, we must incorporate relativistic effects [4]. We develop Autschbach's zeroth-order regular approximation (ZORA) scalar-relativistc theory of J-coupling [5] inside a PAW framework to give a highly efficient, zero-cost, extension to the method to predict J-coupling in systems containing heavy atoms.

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First-principles calculation of Seebeck coefficient of $AgSbSe_2$

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The electronic structure of $AgSbSe_2$ in four different crystal structures is calculated in the framework of density functional theory and generalized gradient approximation (GGA) by using pseudopotential technique. Then the electronic structure of the more stable structures is used to calculate their Seebeck coefficient in the framework of Boltzmann theory of semiclassical transport. In order to correct the wrong metallic behavior of the systems within GGA, a scissor shift is applied to the calculated electronic structures. Calculating the Seebeck coefficient at various energy band gaps and carrier concentrations and then comparing with the experimental data, evidences a structural phase transition of $AgSbSe_2$ at temperatures of about 250K. Our results show that the fast reduction of the Seebeck coefficient at temperatures above about 600K, observed in experiment, may be attributed to the thermally induced electronic excitations.

Main Topic: T4   Quantum Monte Carlo

Study of Vanadium- and Cobalt-Benzene Half-Sandwich Arenes by Stochastic Quantum Sampling Approach

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A multi-stage modeling based on density functional theory (DFT) and quantum Monte Carlo (QMC) approaches, allowing a consecutive elimination of systematic biases except for the fixed-node error in QMC, enabled us to determine the structure, spin multiplicity, vertical and adiabatic ionization potentials, dissociation energy, and spin-dependent electronic gaps of the neutral vanadium- (VBz) and cobalt-benzene (CoBz) half-sandwich arenes. Studied molecules are of importance e.g. in molecular synthesis, catalysis, and potentially in spintronic applications. Ground-state spin multiplicities were deduced from the total energies (CoBz) and their combination with vertical ionization potentials (VBz), since total energies alone were not conclusive here due to their near-degeneracy (cf. Fig. 1). The spin gaps for VBz were found to exhibit different values for the two spin channels, whereas for CoBz, the gaps were found to be comparable. The former molecule may thus be utilized as a spin valve. The overall results differ from the established picture based on previous less accurate calculations, pointing to the importance of accurate many-body treatment of electronic correlation effects in predictive calculations of organo-metallic compounds containing transition metals, such as those studied in the presented work.

FIG. 1. Relative energies of VBz in doublet, quartet and sextet spin states from DFT and QMC.

Applications:
A3 Magnetism and Spintronics

Performance of local orbital basis sets in the self-consistent Sternheimer method for dielectric screening of extended systems

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We investigate the performance of the numerical pseudo-atomic basis of the SIESTA package for the calculation of the dielectric screening of extended systems. The dielectric matrix is calculated with the self-consistent Sternheimer method [1], which does not need an explicit sum over conduction states. To asses the quality of the basis sets we compare results to standard planewave calculations using the same computational parameters. We show results of the frequency-dependent dielectric function for the semiconductors diamond, silicon and germanium, thus covering a range of materials with more insulating to more metallic character [2]. The dielectric constants obtained with our method are in very good agreement with the reference planewaves calculations [3]. We also show preliminary results for the GW self-energy of silicon obtained by calculating the screened Coulomb interaction and the Green's function using local orbitals.

This work is funded by the European Research Council under the European Community's Seventh Framework Programme, Grant No. 239578, and Spanish MICINN Grant FIS2009-12721-C04-01.

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The GW approximation in GPAW

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We present the implementation of the GW approximation [1] within the GPAW electronic structure code [2,3]. The GW method arises from many-body quantum theory and resolves some of the main drawbacks of standard DFT, like the well-known bandgap problem and the descripition of Van-der-Waals interactions. Over the last years, it has been successfully used for a large variety of systems and applications.

The performance of our implementation is tested for the calculation of quasiparticle bandstructures of a number of common semiconductors and insulators and compared with DFT and especially with the commonly used GLLBSC functional. We find that even the so called "one-shot GW" based on the plasmon pole approximation for the dielectric function gives bandgaps in very good agreement with experiment.

As one example for a 2-dimensional system, we calculate the electronic structure of graphene on boron-nitride. Here, the GW approximation turns out to describe the screening effects between the two single layers correctly, which is not the case within standard DFT.

We also calculate the ionization potentials for a set of small molecules as a test case for finite structures. Special focus is set to convergence with respect to the planewave basis and number of unoccupied bands.

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Enhanced metallicity in armchair graphene nanoribbons with Cu impurities

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First-principles calculations have been employed to investigate the effect of Cu impurities on the transport properties of armchair graphene nanoribbons (AGNR). Pristine ribbons have also been investigated for the comparison basis. Our considered structures include one-edge Cu-terminated AGNR, substitutional edge Cu-doped and substitutional centre Cu-doped AGNR. We calculated transmission spectra (TS) and the current-voltage (*I-V*) relationships as shown in Fig. 1(a) and 1(b) respectively. Present TS calculations revealed the semiconducting nature of pristine ribbons. One-edge Cu-terminated ribbons are found narrow band gap semiconductors, on the other hand high transmission coefficients at Fermi level indicate purely metallic character of Cu-doped AGNR. The similar behaviour is further supported by the *I-V* relationship of considered configurations exhibiting high current values for Cu-doped configurations. The results suggest a convenient way of tuning the metallicity of AGNR merely by controlling the site of Cu impurity. The observed high metallicity makes ribbon a potential candidate for interconnects in nanoelectronic devices and various other technological applications.

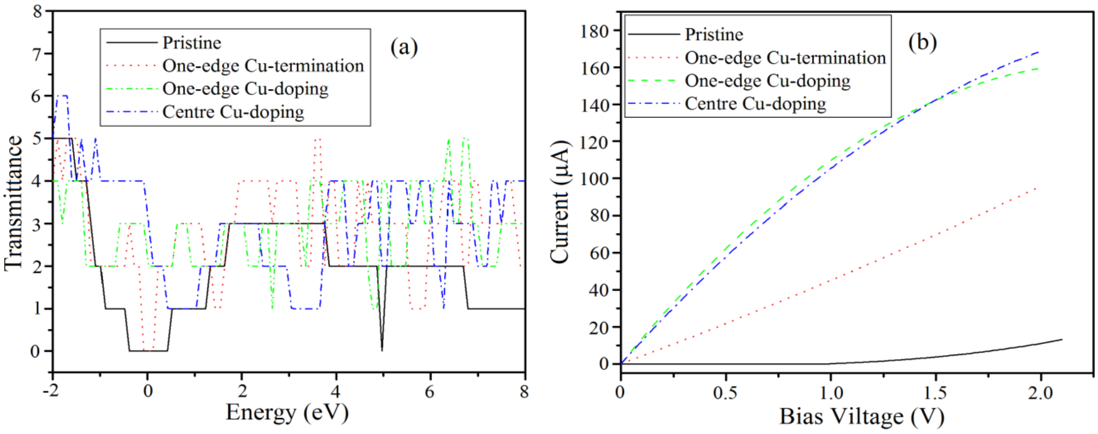

Fig. 1- (a) Calculated transmission spectra (TS) and (b) The current-voltage (*I-V)* relationship for pristine and Cu-containing AGNR.

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Quasi-linear band structure and electronic transport in transparent conducting oxides

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There have been a great many interests in transparent conducting oxides (TCOs) such as ZnO, In_2O_3, and SnO_2 due to their superior optical transparency and electrical conductivity, which leads to various optoelectronic applications. Recently, studies on amorphous compounds of TCOs such as $InGaZnO_4$ (IGZO) have been attracting a great deal of interests due to their application as high-mobility channel layer in TFT, and therefore, it is expected to alter the amorphous Si in the near future. Even though many studies have emphasized that the spherical symmetry and the large size of s orbitals of metal ions mainly contribute to the high electronic mobility, full microscopic understanding has not been achieved yet. In particular, first-principles calculations confirm that oxygen p orbitals are also important for low-energy structure of conduction bands in TCOs.

In this study, we apply a tight binding (TB) approximation to analyze the conduction bands of crystalline or amorphous TCOs. We explicitly consider oxygen s and p orbitals in addition to metal s orbitals. We identify parallel or isotropic coupling conditions which are inherent in the local configurations found in most TCOs. The result of TB model shows that the conduction bands of TCOs show the dispersion relation of massive Dirac particles ($E = \sqrt{\epsilon^2 + \gamma^2 k^2}$). As such, linear-dispersion bands appear at high energies or high carrier densities. The linear dispersion relation is a result of overlap integral between metal s and oxygen p orbitals. As an application of our model, we evaluate the electronic mobility of single crystalline ZnO by considering ionized impurity scattering and optical phonon scattering. It is found that the mobility has a minimum value at the carrier density of 10^{19}cm^{-3} which is in good agreement with experiment.

Main Topic: T10 Simulations in Realistic Environments

Radiation damage in biological systems: Ab initio MD studies”

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DNA damage cause by irradiation has been studied for many decades. Motivations include assessing the dangers posed by radiation, and understanding how to improve the efficiency of radiotherapies in combating cancer. Surprisingly, low-energy electrons (<3 eV) play an important role in this damage. This work aims to understand the behavior of DNA components in the condensed phase, due to the presence of such electrons.

We conducted ab initio molecular dynamics simulation studies of an excess electron in condensed phase models of DNA nucleobases, nucleosides and nucleotides. The main result is that vertically attached electrons rapidly (<15 ns) localize in the bases (GCAT), which have an adiabatic affinity of around 1 eV. Nucleotides do not cleave spontaneously upon electron addition, but our calculated free energy barriers are low enough to support the cleavage as a regular feature at room temperature. This process, however, is competitive with protonation of the base. We also present some preliminary results on solvated trinucleotides and base pairs, as well as nucleobases solvated in glycine instead of water.

Electronic correlations and crystal structure distortions in $BaBiO_3$

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$BaBiO_3$ is a material where formally Bi^{4+} ions with the half-filled 6*s*-states form the alternating set of Bi^{3+} and Bi^{5+} ions resulting in a charge ordered insulator. The charge ordering is accompanied by the breathing distortion of the BiO_6 octahedra (extension and contraction of the Bi-O bond lengths). Standard Density Functional Theory (DFT) calculations fail to obtain the crystal structure instability caused by the pure breathing distortions. Combining effects of the breathing distortions and tilting of the BiO_6 octahedra allows DFT to reproduce qualitatively experimentally observed insulator with monoclinic crystal structure but gives strongly underestimate breathing distortion parameter and energy gap values. In the present work we reexamine the $BaBiO_3$ problem within the GGA+U method using a Wannier functions basis set for the Bi 6*s*-band. Due to high oxidation state of bismuth in this material the Bi 6*s*-symmetry Wannier function is predominantly extended spatially on surrounding oxygen ions and hence differs strongly from a pure atomic 6*s*-orbital. That is in sharp contrast to transition metal oxides (with exclusion of high oxidation state compounds) where the major part a of *d*-band Wannier function is concentrated on metal ion and a pure atomic *d*-orbital can serve as a good approximation. The GGA+U calculation results agree well with experimental data, in particular with experimental crystal structure parameters and energy gap values. Moreover, the GGA+U method allows one to reproduce the crystal structure instability due to the pure breathing distortions without octahedra tilting.

Magnetic Spectroscopies with DFT + Hubbard (U,V)

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Hubbard U corrections to local or semi-local exchange-correlation functionals, first introduced to deal with the physics of correlated electrons [1], have been shown to greatly improve the accuracy of standard DFT calculations in molecular systems containing transition-metal ions [2], thanks to their ability to restore piecewise linearity in the energy as a function of occupation numbers [3] and thus correct self-interaction errors of approximate exchange-correlation functionals. In addition, the linear-response formulation of Cococcioni and de Gironcoli [3] allows to consider U not as a fitting parameter, but as a truly first-principles response function of the system considered.

Nevertheless, transition-metal complexes that display both covalent and ionic character are poorly described by DFT+U [4]. Recently, the addition of an intersite Hubbard term V is suggested to be able restore the high accuracy of DFT+Hubbard also in partially covalent cases [4,5], while allowing the calculation of V in a linear-response fashion [5].

In this study we combine the DFT+U+V approach with the gauge-invariant projector augmented wave method (GIPAW) [6], to deal with the calculation of magnetic spectroscopies. We have been implementing this combination in the Quantum ESPRESSO distribution [7], using the recently introduced converse approach [8,9], that substitutes the use of perturbation theory with a much simpler Berry-phase calculation of the orbital magnetization. We then examine the performance of U+V approach in determining the structural properties and hyperfine interaction parameters of simple transition-metal molecules and complex organometallic systems.

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Infulence of exchane-correlation functional on local order competition in disordered phase of $Ge_2Sb_2Te_5$: octahedral versus tetrahedral Ge

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$Ge_2Sb_2Te_5$ (GST) is a key material used in rewritable phase-change optical memories and phase-change random access memories. The understanding on the local order in amorphous structures would be not only fundamentally intriguing but also technologically important to resolve various technological hurdles. Several studies have been carried in this direction, but unfortunately there is serious discrepancy between first-principles results and the extant experimental observations. In particular, Ge-Te distance is longer than experimental values by 0.1 0.2 A in both liquid and amorphous structures. This is closely related to the fact that semilocal functionals tend to favor octahedral Ge atoms. Being similar to the crystalline bonding geometry, the octahedral Ge atoms lead to more delocalized electrons. However, in disordered systems such as liquid and amorphous phase, the electrons at band edges are inherently localized and chemistry-based functionals such as BLYP or Hatree-Fock can be better choices.

In this presentation, we discuss on the liquid and amorphous structures of GST studied with molecular dynamics simulations using various exchange-correlation functionals such as PBE, BLYP, and HSE06 with 0.25 and 0.5 mxing parameter. We confirm the previous conclusion that the PBE functional results are at variance with the experimental data as mentioned above. On the other hand, the hybrid functionals significantly increase the population of t-Ge atoms and the liquid structures are in much better agreement with experiment compared to results with semilocal functionals. This implies that the chemistry-based functionals such as hybrid functionals might better describe the disordered systems than PBE. The amorphous structures are obtained through the melt-quench process and hybrid functionals produce amorphous structures that satisfy 8-N rule more closely than semilocal functionals. Lastly, we examine relative preference between octahedral and tetrahedral Ge atoms by using random phase approximation (RPA) method based on adiabatic conection fluctuation dissipation theory (ACFDT) for which it is believed that the accuracy is higher than semilocal or hybrid functionals.

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Ab-initio Sternheimer-GW method for quasiparticle calculations

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During the past few years the GW method has emerged as the *de facto* standard for investigating electronic excitations in bulk and nanoscale systems. Significant efforts have been devoted recently to extending the range of applicability of the GW method to large and complex systems. Within this framework Ref. [1] has introduced a methodology for performing GW calculations using the self-consistent Sternheimer equation. In the method of Ref. [1] the screened Coulomb interaction and the non-interacting Green's function are calculated without using unoccupied Kohn-Sham states, in the same spirit as density-functional perturbation theory. The method of Ref. [1] was demonstrated in a planewaves basis set implementation using empirical pseudopotentials. In the present work we extend the method of Ref. [1] to the case of fully *ab-initio* calculations using planewaves and norm-conserving or ultrasoft pseudopotentials [2]. In the present implementation the screened Coulomb interaction is evaluated on the imaginary frequency axis and analytically continued to the real axis using Padé approximants, and the Green's function is evaluated directly along the real axis. These choices allow us to construct the complete position- and energy-dependent GW self-energy operator, and make the calculation of the entire (G0W0) quasiparticle spectral function computationally accessible. We have validated our methodology by calculating the quasiparticle band structures of standard semiconductors and insulators (Si, SiC, diamond, LiCl) and by comparing the results with previous GW calculations.

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Strongly-correlated quantum wires within Kohn-Sham Density Functional Theory

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We use the exact strong-interaction limit of the Hohenberg-Kohn energy density functional to approximate the exchange-correlation energy of the restricted Kohn-Sham scheme. This allows us to construct a highly non-local density functional whose functional derivative can be easily obtained and that transforms, in a physically transparent way, an important part of the electron-electron interaction into an effective local one-body potential. Our calculations on quasi-one-dimensional quantum wires show that our approach captures essential features of the strongly-correlated regime that are out of the reach of the currently available functionals within restricted Kohn-Sham Density Functional Theory.

Disorder effects in solid state systems beyond a single-site prospective: theories and applications.

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We review development and applications of improvement attempts upon the original Coherent Potential Approximation (CPA) for the treatment of disordered systems. The single-site theory is reviewed in its basic aspects of analiticity and convergence, and compared with alternative methods for the study of solid state systems where a rigorous application of Bloch's theorem is no longer possible.
The aspects of local environment effects, short-range ordering and off-diagonal disorder are examined in different extension proposals, in tight-binding and first-principles illustrations based on multiple-scattering theory. In this context, results from application of a generalized version of the method are discussed in the evaluation of disorder effects in solid state metallic solutions, molar doping materials for fuel cell technology, and magnetic compounds and excitations. Results from alternative methodologies such as supercell or special quasi-random structure (SQS) approximations are also examined.

Efficient evaluation of Fock exchange for non-localized wave-functions

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In density functional theory (DFT), hybrid functionals for the exchange and correlation energy which include an exact exchange term are increasingly becoming more popular and are already the most used in quantum chemistry applications. Indeed, exchange integrals can be conveniently calculated in the case of quantum chemistry approaches which are based on the expansion of the Kohn-Sham wave-functions on localized basis sets. In contrast, when wave-functions are expanded on plane-waves, as common in most of the approaches for extended materials, the evaluation of such terms is more demanding in terms of computational resources.

We introduce an approach which permits to significantly reduce the computational cost for the evaluation of the Fock exchange operator when it is applied to an arbitrary periodic wavefunction in the case of large simulation cells. This method is based on the exponential decay properties of the density matrix and can be applied to systems exhibiting a finite electronic gap. We first validate and benchmark the approach on the isolated benzene molecule and then we apply it to the isolated tetraphenylporphyrin molecule (C44H30N4) and to a model of bulk Si comprising 512 atoms. We show that final speed-up factors of more than 5 for the entire self-consistent calculation using hybrid-functionals can be reached, while the Fock routines only are up to 10 times faster. Our scheme does not require the evaluation of Wannier's functions and can be easily implemented in density-functional theory codes based on plane-waves.

Polyamorphism in CO_2 from *ab initio* molecular dynamics

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We studied behavior of amorphous carbon dioxide under pressures up to 100 GPa and temperatures ranging from 200 to 500 K by means of *ab initio* molecular dynamics. We found several different amorphous phases and focused on analysis of respective structural properties. Upon compression of molecular crystalline phase III we found the previously known non-molecular amorphous form with three and four-coordinated carbons. Upon decompression of this phase we observed several other possible phases with different proportion of three and four-coordinated carbons and containing also CO_2 molecules. Final product of the decompression to low pressure is the molecular amorphous phase, in agreement with experiments.

Z-method calculation of the Mg melt curve

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The Z-method has been using to calculate the melting curve of magnesium to high pressure. The calculations were performed using the VASP code within the generalized gradient approximation. In the simulations, transitions to the liquid from both the hcp and bcc phases have been considered. Generally, it has been found that the agreement between theory and experiment is very good. However, indications have been found which suggest that, at a given pressure, the solid melts over a range of temperatures. As a consequence, it may be the case that the Z-method is able to provide only an upper and lower bound to the melt curve.

Structural and orbital phase transitions induced by Jahn-Teller distortions in $KCuF_3$

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We study the melting of the cooperative Jahn-Teller distortion in $KCuF_3$. To properly describe this order-disorder transition we have to work with large real-space cells. For this we use a combination of first-principle calculations (LDA+U) and Monte Carlo (MC) simulation. First we determine the potential energy surface for displacements of the fluorine ions. Subtracting the long-ranged Coulomb terms leads to a short-ranged parametrization of the dynamical matrix for pairs of fluorine displacements. We then use the parametrized LDA+U energies as the input for Monte Carlo simulations of extended supercells to study the spatial range of the lattice ordering as a function of temperature.

Main Topic: T1 Density-Functional Theory beyond LDA

Extension of the SCE Formalism to Fractional Electron Numbers and Investigation of the Derivative Discontinuity

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Despite the tremendous success of density functional theory (DFT), approximate exchange-correlation functionals are yet not able to capture the full palette of properties of interest for chemistry and solid state physics[1]. Strong correlation, as it occurs in bond stretching situations and Mott insulators, constitutes some of this challenges. The strong interaction limit of DFT offers a promising path towards the proper inclusion of strong correlation phenomena in density functionals.

In this poster we show how the strictly-correlated electrons concept (SCE)[2] can be applied to improve Kohn-Sham DFT[3]. We formulate an SCE for fractional electron numbers and investigate the derivative discontinuity of the energy[4]. Therefore we study 1-dimensional chains of fractional densities, where an exact SCE solution can be found. A model is then derived, capable of exactly reproducing the exact results. The model is subsequently applied to 3-dimensional spherical densities and a derivative discontinuity is shown for the Hydrogen and Lithium external potential.

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Doping at the Si-SiO$_2$ interface

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The Si-SiO$_2$ interface is a common feature in modern silicon-based complementary metal-oxide-semiconductor (CMOS) technology for the fabrication of integrated circuits. Due to the ongoing miniaturisation drive for such devices, it is becoming increasingly important to understand the effect of the interface on the dopant distribution and properties. Indeed, in some modern integrated circuits, channel lengths have been reduced to a few tens of nanometres, with the device properties being determined by only about 100 dopant atoms.

We have investigated the properties of arsenic dopants at the Si-SiO$_2$ interface. We use a large supercell to simulate both ordered (α-cristobalite) and disordered interfaces. The disordered interface is generated using a multiscale approach in which a Monte Carlo method is parametrised with density-functional theory calculations and is used to access the long time scales required for amorphising the oxide. The segregation of arsenic dopants in silicon at the interface structure is then studied using DFT.

The large size of our systems allows us to accurately characterise the long-range quantum confinement effect due to the interface, which is found to result in a small energy barrier for segregation. We also investigate the effect of the local stress at the defect site on its segregation energy, and show that a simple ‘particle in a box’ model can be used to explain the calculated segregation energies at all substitutional silicon sites, independently of the oxidation state.

Topological surface state scattering in Antimony

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In this work we study topologically protected states on the Sb(111) surface by using *ab-initio* transport theory. In presence of a strong surface perturbation we obtain standing wave states resulting from the superposition of spin polarized surface states. By Fourier analysis, we identify the underlying scattering processes and the spin texture. We find evidence of resonant transmission across surface barriers at quantum well states energies and evaluate their life-times. Our results are in excellent agreement with experimental findings. We also show that despite the presence of a step edge along a different high symmetry direction, not yet probed experimentally, the surface states exhibit unperturbed transmission around the Fermi energy for states with near normal incidence.

Spin transport and magnetic behavior of boron nitride nanoribbons with magnetic impurities

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Ab initio calculations are performed in the framework of density functional theory on Mn-doped boron nitride sheets, which are candidates for two-dimensional diluted magnetic semiconductors (DMSs). Each type of substitution reveals a qualitatively different magnetic behavior encompassing ferromagnetic, anti-ferromagnetic and spin glass ordering. The ability of formation of these defects is also discussed. We analyze the dependence of the exchange couplings on the distance between impurities and the typical range and distribution are extracted. Multiple-impurity configurations are considered and the results are mapped on an Ising-type Hamiltonian with higher order exchange interactions, revealing deviations from the standard two-spin models. The percolation of interacting magnetic moments is discussed and the critical concentration is determined for the underlying transition from a ferromagnetic to a super-paramagnetic state. We conclude our study by providing the optimal conditions for doping in order to obtain a ferromagnetic DMS [1]. I also investigate the spin transport in boron nitride nanoribbons with magnetic impurities. The first principle approach based on non-equilibrium Green’s functions gives the polarization of the spin current for different structures and biases [2]. Several spin configurations of the magnetic impurities are considered, revealing different behaviors in the spin resolved current. Some key aspects regarding spin switching effects, i.e. the turning on and off the net spin current at different biases, are also discussed. The experimental availability of the building blocks -- hybrid boron-nitrogen-carbon (BNC) materials -- as well as the magnitudes of the obtained spin current polarizations indicates a strong potential of the analyzed structures for future spintronic devices.

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Theory and Methods:
T8 Electronic Transport
Applications:
A1 Nanoscience
A3 Magnetism and Spintronics

Photoemission spectroscopy from Koopmans' compliant functionals, and its application to the tautomeric populations of DNA and RNA nucleobases

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We study the structural and photoelectron properties of five DNA and RNA nucleobases - guanine (G),adenine (A), cytosine (C), thymine (T), and uracil (U) - using either the Perdew-Zunger self-interaction correction [Phys. Rev. B 23, 5048 (1981)] or Koopmans' compliant functionals [Phys. Rev. B 82, 115121 (2010)]. We also report on the implementation of a simple method for simulating photo-emission spectra from molecules, based on a plane-wave approximation for the final states to account for the transmission matrix within the DFT. Finally, the photo-emission spectra are modeled by summing individual tautomer spectra weighted by Boltzmann population ratios of the tautomers - in themselves in good agreement with experimental results. Our calculations show that the Koopmans' compliant functionals provide vertical ionization energies compatible with the values computed by high-accuracy quantum chemistry methods (see in [Phys. Rev. B 84, 075103 (2011)] and the references therein), and spectra that are in remarkable agreement with experimental results.

Spin state transition in $LaCoO_3$: a DFT+DMFT aproach

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An $LaCoO_3$ system is a subject of interests a lot of scientists for over half a century [1-3]. Currently one of the major open questions is that which atomic multiplets responsible for a formation of an local magnetic moments on Co ion? To find an answer to this question a combination of a density functional theory and a dynamical mean-field theory (DFT+DMFT) had been applied [4]. The algorithm of statistical analysis of an atomic states had been developed and implemented. To account a strong covalent bond a spin states of Co ion have been generalized to the case including not only d6 but also d7 and d8 electronic configurations. Presence the d7 and d8 states causes a decrease of the effective moment value to magnitude about 3.5 μ_B.

The results of the study allow us to suggest the following description of physics of spin state transition in $LaCoO_3$ compound. At the lowest temperatures $LaCoO_3$ is in the low-spin state (LS) containing some number of isolated ions in the excited high-spin state (HS). Growth of a temperature accompanied by a positive feedback from the crystal lattice leads to increase the number of sites in HS state and to formations of HS-LS short-range order which is responsible for insulator behaviour in the temperature range 100-500K. The second transition near 500K is associated with the destruction of the HS-LS order which leads to abnormal expansion of the crystal lattice due to the destruction of HS-LS relationships.

Experimentally observed transition to the metallic phase changes the character of the local moment states mixture from mixed intermediate-like spin state (IS) to the dominant HS configuration.

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Frequency-dependent Hubbard U corrections to DFT: A simple approach

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When the Hubbard Hamiltonian is coupled with first-principles methods such as DFT, as it is in DFT+U and DFT+DMFT, the Hubbard U parameters may be interpreted as the tensor elements of the screened Coulomb interaction in the basis of projector functions spanning a set of spatially-localised subspaces. The best choice of projector functions to be used, and screening mechanisms to be included (or, conversely, constrained out) are non-trivial matters, and genuinely depend on the nature of the Hamiltonian, and its solver, with which the U is to be used. Since the screening of charge is a dynamical process, in any case, it is clear that the Hubbard U must take on a frequency dependence in order to realise the full capability of existing methods such as DFT+U and DFT+DMFT, necessitating their generalisation in order to accommodate a $U(\omega)$, but likely further improving the resulting spectra with respect to experiment.

We propose a simple approach to computing and employing the $U(\omega)$, in the spirit of both the density-functional linear-response approach to DFT+U and the perturbative GW approximation, which is suitable for implementation within an existing DFT+U or constrained DFT code. We reformulate the linear-response approach for the static U in the language of many-body perturbation theory, where its relationship to methods such as constrained RPA, and its generalisation to the dynamical case, become evident. We propose a simple plasmon-pole type model for the subspace inverse dielectric function, in which the low-energy parameters are obtained from linear-response DFT+U, appropriately renormalised, and the high-energy parameters are computed using an inexpensive technique such as independent-particle RPA. We derive new, rotationally-invariant "DFT+$U(\omega)$" self-energy expressions that capture attractive features of both DFT+U and GW, and which reduce and extend, respectively, to each. In the first instance, we use first-principles Wannier functions to study our "DFT+$U(\omega)$" perturbatively.

Extending the random-phase approximation for electronic correlation energies: The renormalized adiabatic local density approximation

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The adiabatic connection fluctuation-dissipation theorem with the random phase approximation (RPA) has recently been applied with success to obtain correlation energies of a variety of chemical and solid state systems. The main merit of this approach is the improved description of dispersive forces while chemical bond strengths and absolute correlation energies are systematically underestimated. In this work we extend the RPA by including a parameter-free renormalized version of the adiabatic local density (ALDA) exchange-correlation kernel. The renormalization consists of a (local) truncation of the ALDA kernel for wave vectors $q>2k_F$, which is found to yield excellent results for the homogeneous electron gas. In addition, the kernel significantly improves both the absolute correlation energies and atomization energies of small molecules over RPA and ALDA. The renormalization can be straightforwardly applied to other adiabatic local kernels.

Wavelets and Projector Augmented-Wave approach: an adaptive basis set for large-scale calculations at all-electron accuracy.

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Wavelets are a systematic and adaptive basis set which have been implemented into two DFT codes: BigDFT [J. Chem. Phys. 129 (2008) 014109], a massively parallel code for calculations in large systems, and ABINIT [Comput. Phys. Commun. 180 (2009) 2582], a world-reknowed software for total-energy calculations. On the other hand, the projector augmented-wave (PAW) method [Phys. Rev. B 50 (1994) 17953] has been widely used due to its inherent all-electron (AE) accuracy and the use of ultra-soft pseudo-potentials. In this work we detail the implementation of a mixed wavelets & PAW basis set into ABINIT and BigDFT. The resulting code has proven highly successful with the systematic and adaptive characteristics of wavelets and the PAW AE precision. Preliminary tests on our mixed wavelets-PAW code and on the well-stated plane-wave-PAW code (implemented in ABINIT) show the same accuracy up to machine precision.

A new field-theoretic approach to linear scaling ab-initio molecular dynamics

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For large systems the calculation of the electronic structure of atoms and molecules is fairly expensive. For that reason developing methods that scale linearly with respect to the size of the system is a desirable aim.

On that account we present an alternative field-theoretic method suitable for linear scaling molecular dynamics simulations using forces from self-consistent electronic structure calculations. It is based on an exact decomposition of the grand canonical potential for independent fermions and does neither rely on the ability to localize the orbitals nor that the Hamilton operator is well-conditioned. Hence, this scheme enables highly accurate all-electron linear scaling calculations even for metallic systems. The inherent energy drift of Born-Oppenheimer molecular dynamics simulations, arising from an incomplete convergence of the self-consistent field cycle, is solved by using a properly modified Langevin equation.

The predictive power of this approach is illustrated using the example of liquid methane at planetary conditions. Methane occurs in the middle ice layer of the giant gas planets Uranus and Neptune. In this layer, at a depth of one-third of the planetary radius, pressure and temperature range from 20 GPa and 2000 K to 600 GPa and 8000 K which we simulate by means of large-scale electronic structure based molecular dynamics using our method. We address the controversy of whether or not the interior of Uranus and Neptune consists of diamond. We find no evidence for the formation of diamond, but rather carbon chains and sp^2-bonded polymeric carbon. We predict that at high temperature hydrogen may exist in its mono-atomic and metallic state.

Optical Absorption in B_{19}^- Cluster : A Time Dependent Density Functional Approach

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The linear optical absorption spectra of different isomers of planar boron cluster B_{19}^- are calculated using time-dependent spin-polarized density functional approach. The geometries of these cluster are optimized at the B3LYP/6- 311+G* level of theory. Even though the isomers are almost degenerate, the calculated spectra are quite different, indicating a strong structure-property relationship. Therefore, these computed spectra can be used in the photo-absorption experiments to distinguish between different isomers of a cluster.

Recent progress in the theory of flexoelectric response

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Flexoelectricity is the linear polarization response of an insulator to a strain gradient. Unlike piezoelectricity, flexoelectricity is symmetry-allowed in any insulator. Although hardly detectable in macroscopic samples, this effect has attracted considerable interest from the experimental community in recent years, as nanoscale geometries (where huge strain gradients can occur) hold concrete promise for practical device applications.

From the theoretical point of view, however, a comprehensive theory is still lacking, despite some notable recent achievements. In this presentation I will show how to overcome some of the remaining formal difficulties, e.g. concerning the relationship between dynamical and static coefficients, and the electronic versus lattice-mediated effects. As a proof of concept I will present a complete ab-initio calculation of the full flexoelectric tensor in a simple rocksalt solid, NaCl.

Strong Isotope effect in phase II of Dense Solid Hydrogen and Deuterium

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The role of quantum nuclear zero-point motion in the structural changes of solids H_2 and D_2 under pressure is investigated for the low-temperature phases and around the melting curve by first-principles path-integral molecular dynamics (PIMD) calculations [1]. A revision of the current interpretation of the nature of phase II as well as an isotope difference is presented. Molecular orientations are well defined in phase II of D_2, while solid H_2 exhibits large and very asymmetric angular quantum fluctuations in this phase, with possible rotation in the (bc) plane, making it difficult to associate a well-identified single classical structure. The mechanism for the transition to phase III is also described. Existing structural data support this

We have used the ABINIT code [2], in which we have implemented the path-integral formalism for nuclei. For the sake of numerical efficiency, we have introduced in ABINIT, beyond the already existing levels of parallelization, an additional level of parallelization which has a quasi-linear scalability. It allowed us to perform very long DFT-PIMD trajectories of at least 30 000 steps, and up to 100 000 steps in some cases where a high level of statistics was required.

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Computer simulation of the reaction mechanism of matrix metaloprotease MMP3 by QM/MM methods

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The matrix metalloproteinases (MMP) constitute a family of zinc (Zn) proteases that catalyze the breaking of peptide bonds in proteins, and a very promising target in drug therapy.It is suggested that a conserved water molecule is essential for the catalysis, where the nucleophillic attack is assisted by water deprotonation, performed by a conserved glutamate. Nevertheless, there’s also evidence for a direct nucleophillic attack by the enzyme, performed by the same glutamate. There are also other propositions, suggesting the participation of more than one water molecule in the reaction. Thus, the precise role of Zn in the catalyzed reaction and the coordination environment around it is not fully defined yet. In this work, we use hybrid quantum/classical calculations to evaluate the reaction barrier by the two suggested mechanisms. Our results support the water mediated mechanism, where the carbonyl oxygen of the scissile peptide bond is coordinated to zinc, but the attacking water molecule is not necessarily coordinated to zinc in the initial step, and the hydrogen of the water is transferred to the glutamate side chain as the water attack progresses. Coordination of a second water to the substrate carbonyl oxygen is not also a requirement, as suggested by other studies. Also, the water oxygen attack and the peptide carbon-nitrogen bond breaking are stepwise events, with a well-defined tetrahedral intermediate, and the corresponding calculated barriers were 15,9 kcal/mol and 15,1 kcal/mol. The overall barrier found is in good agreement with experimental data for other zinc-metalloenzymes.

<u>Applications</u>:
A1 Nanoscience
A2 Biochemistry and Biomaterials
A8 Catalysis and Electrochemistry
A9 Chemical Reactions and Kinetics

Towards Petascale DFT-calculations: a new parallelization approach for linear response and exact exchange

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Simulating complex materials and biological systems is nowadays a big challenge despite the availability of supercomputers. One of the most promising techniques used for study the properties of these systems is based on Density Functional Theory approach and its extension. This technique is widely used in solid state physics where the sample is usually periodic. Unfortunately disordered solids and biophysical systems cannot be treated by using this assumption so a large supercell it is necessary.

Here I present a new parallelization approach aimed to overcome the limit of the traditional parallelization approach in plane-waves DFT codes. In the framework of PRACE I&II IP a new parallelization strategy over the electronic bands has been introduced. In order to show the efficacy of this approach two challenging kernels has been identified: the linear response (used to compute NMR spectra) and the Exact-Exchange (to evaluate the Fock exchange operator, in hybrid-DFT functionals). Those two kernels are well isolated inside the Quantum-ESPRESSO distribution, and are constituted by several nested loops. Moreover, they are very time consuming, and any improvement towards increasing their scalability, is going to show up in the total wall time execution.

The benchmark results I report, prove that this parallelization approach achieve good scaling on many thousands of CPUs, and strongly advise to spread the band parallelization to the whole QE package. This strategy is a breakthrough in plane-waves DFT codes and it will be mandatory to fully exploit the petascale hardware and beyond.

Kohn-Sham orbitals from Quantum Monte Carlo Density

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In this work we explore the possibility to extract kinetic energies, orbitals, orbital energies and exchange correlation potentials from accurate Quantum Monte Carlo densities for atomic systems Helium, Beryllium, Neon and molecules. The Quantum Monte Carlo densities are calculated both at variational level (VMC) using accurate Jastrow Antisymmetrised Geminal Power (JAGP) wave functions and at lattice regularized diffusion Monte Carlo (LRDMC) level. Starting from these densities, we extract the Kohn-Sham quantities using the method developed by Zhao et al. (Phys. Rev. A 50, 2138 (1994)). We find reasonable agreement with results obtained from CISD densities for the calculated exchange-correlation potentials and ionization energies, indicating that QMC densities can be successfully used for the development of improved approximate functionals and for the practical application of embedding schemes based on DFT.

Ab initio angle- and energy-resolved photoelectron spectroscopy with time-dependent density-functional theory

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We present a time-dependent density-functional method able to describe the photoelectron spectrum of atoms and molecules when excited by laser pulses. This computationally feasible scheme is based on a geometrical partitioning that efficiently gives access to photoelectron spectroscopy in time-dependent density-functional calculations. By using a geometrical approach, we provide a simple description of momentum-resolved photoemission including multiphoton effects. The approach is validated by comparison with results in the literature and exact calculations. Furthermore, we present numerical photoelectron angular distributions for randomly oriented nitrogen molecules in a short near-infrared intense laser pulse and helium-(I) angular spectra for aligned carbon monoxide and benzene.

Effective Hamiltonians for large-scale *ab-initio* lattice dynamics simulations of perovskites and related materials

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We present *ab-initio* method for rapid evaluation of the total energy of a crystalline system, which allows running simulations spanning thousands of atoms and tens of thousands of simulation steps at small computational cost. Our method extends previous approaches in which a model Hamiltonian with limited degrees of freedom is constructed on basis of full electronic structure calculations[1, 2, 3]. Presented model retains all ionic degrees of freedom and it is capable of representing exactly the *ab-initio* energetics of investigated material up to a second order of energy expansion. Higher order expansion terms of the model are optimised to available *ab-initio* results, with the typical accuracy of a few meV/f.u. The resulting models provide not only the basic energetics of the studied materials, but also their phonon dispersion spectra.

We apply the presented method to two important perovskite materials: $SrTiO_3$ and $PbTiO_3$. Using Monte-Carlo simulations, we calculate temperature dependent properties of these materials, such as spontaneous polarisation, dielectric susceptibility, thermal expansion etc. At the same time, the presented model allows us to investigate microscopic mechanisms for the macroscopic properties. This leads, among others, to deeper understanding of intricate interplay between distortion modes of perovskite materials, which determines properties and transitions between their different phases.

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Calculation of thermoelectric properties from first-principles

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The development of new types of thermoelectric materials with a large figure of merit is mainly driven by the needs for sustainable and clean energy. In this respect first-principles study of thermoelectric properties can help to achieve a better understanding of microscopic mechanisms in transport, which provides insight for discovering new materials.

To study the thermoelectrical properties, we combine the well known Boltzmann transport theory with the predictive power of density functional calculations. With the exception of the lattice thermal conductivity, all of the required transport coefficients can be obtained using the BoltzTrap code[1], based simply on the electronic band energies. However, this approach is limited by the hypothesis of a constant relaxation time. To go beyond the relaxation time approximation, we have implemented a first-principles algorithm within the ABINIT package[2] to calculate transport coefficients in solids limited by electron-phonon interaction. As a first step, we study metals, where a solution to the Boltzmann equations based on a variational method is adopted[3]. The calculated electrical conductivity is in excellent agreement with measured data, whereas the Seebeck coefficient is less satisfactory. Besides the missing contribution from phonon drag, which is only important at low temperature, an accurate density of states around Fermi energy is vitally important.

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Optimized Structure and Vibrational Properties by Error Affected Potential Energy Surfaces

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The precise theoretical determination of the geometrical parameters of molecules at the minima of their potential energy surface and of the corresponding vibrational properties are of fundamental importance for the interpretation of vibrational spectroscopy experiments. Quantum Monte Carlo (QMC) techniques are very accurate and promising methods for the electronic structure investigation of correlated systems, but they are intrinsically affected by stochastic errors on both energy and force calculations. This makes the QMC calculations more challenging with respect to other more traditional quantum chemistry tools. To circumvent this drawback in the present work we formulate the general problem of evaluating the molecular equilibrium structures, the harmonic frequencies and the anharmonic coefficients of an error affected potential energy surface. The proposed approach, based on a multidimensional fitting procedure, is illustrated together with a critical evaluation of systematic and statistical errors. We observe that the use of forces instead of energies in the fitting procedure reduces the the statistical uncertainty of the vibrational parameters by one order of magnitude. Several results based on Variational Monte Carlo calculations on the water molecule demonstrate the possibility to evaluate geometrical parameters, harmonic and anharmonic coefficients at this level of theory with an affordable computational cost and a small stochastic uncertainty.[1]

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[1] Optimized structure and vibrational properties by error affected potential energy surfaces. A. Zen, D. Zhelyazov, L. Guidoni, J. Chem. Theory Comput., in press. DOI: 10.1021/ct300576n