

# International workshop on computational physics and materials science

## "Total energy and force methods"

*January, 9 2014 - January 11, 2014*  
*CECAM-HQ-EPFL, Lausanne, Switzerland*

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# 1 Description

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This workshop is a biennial event part of one of the longest-running electronic-structure conference series worldwide: the "Total Energy and Force Methods" workshops (now renamed "Computational Physics and Materials Science"), started in 1984. A major workshop is held biennially at ICTP in Trieste, during odd-numbered years; an alternate workshop (often referred as "mini", but hosting typically 100+ participants) is held on even-numbered years, each time in a different location. The previous most recent workshops took place in Madrid (2000), Tenerife (2002), Paris (2004), Cambridge (2006), Bonn (2008), Shanghai (2010) and Barcelona (2012). This is the first time it is held in Lausanne.

The main idea of this series is to have a smaller scale meeting of around ~100 participants, which serves to review the state-of-the-art worldwide in the field of electronic-structure simulations, and identify interesting new developments and topics. The excellent quality of the scientific program put forward in the past, and the fact that this series represents the traditional appointment dedicated to survey the state-of-the-art in the field, has been the key for the expanding success of these workshops (they have since mirrored by an equivalent series in the US, the "Annual Workshop on Recent Developments in Electronic Structure Methods", started in 1989, and in Asia, with the "ASIAN Workshop on First-Principles Electronic Structure Calculations", started in 1995). The format allows for a close contact of all the participants with the invited speakers and committee members (that also attend the conference).

While the structure of the Trieste workshops is intermediate in size (~300 participants), standing between the very large scale Psi-k conference (~1000 participants or more, but held every 5 years) and small size workshops (~30-50, like those hosted at CECAM), the "mini" workshops have typically an attendance of ~80-100 participants, which, together with its program structure, makes them similar in spirit to traditional CECAM workshops (the workshop would be hosted at EPFL, with CECAM, but would take place in a larger, state-of-the-art auditorium on campus). It also has a strong vocation to attract local students and postdocs, that in Switzerland form a particularly numerous community (close to 20 principal investigators and ~60-70 additional group members in electronic-structure simulations).

The most widespread approaches used in our community, namely in particular DFT, but also TDDFT, GW, DMFT, quantum Monte Carlo, ... provide the foundations for computing many physical and chemical properties of materials. However, there are numerous challenging applications for which the level of approximations used in these implementations or technical limitations are prohibitive for accurate quantitative predictions of materials and devices properties and performance. The goal of the workshop is to give an in-depth analysis of key scientific cases and applications in which the theoretical predictions are limited by methodological or algorithmic issues.

In this respect, the workshop, that focuses on the most recent developments in the field of electronic structure methods from the first-principles perspective and their diverse applications, provides a unique venue, for its size, focus, and history, where to survey and address the state-of-the-art in the entire field of electronic-structure simulations. The choice of topics and lecturers is done in collaboration with the workshop's scientific committee (see below). As in previous editions, the program has around 20-25 invited speakers, during a time span of two and a half days.

The workshop will be structured in thematic sessions in which the oral talks are by invitation. In addition, as it is traditional in this series, a large poster session will take place, which will allow participants to present their work and 'break the ice' to facilitate closer interactions with the invited speakers and committee members.

## 2 Program

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### Day 1 - January, 9 2014

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#### Congregation

- 8:45 to 9:15 – Registration
- 9:15 to 9:30 - Welcome and Introduction

#### Quantum monte carlo - chair Stefano Baroni

- 9:30 to 10:00 - **David Ceperley**  
Which density functionals work for warm dense hydrogen?
- 10:00 to 10:30 - **Cyrus Umrigar**  
Semistochastic quantum monte carlo -- a hybrid of exact diagonalization and quantum monte carlo methods
- 10:30 to 11:00 - Coffee Break

#### Materials design - chair Stefan Goedecker

- 11:00 to 11:30 - **Stefaan Cottenier**  
Dft vs. reality: the error budget
- 11:30 to 12:00 - **Gian-Marco Rignanese**  
Towards a better error assessment of first-principles methods for electronic and optical properties of solids
- 12:00 to 12:30 - **Geoffroy Hautier**  
High-throughput computations as an accelerator for materials discovery: an application to p-type transparent conducting oxides
- 12:30 to 14:30 – Lunch (on your own – see map of EPFL cafeterias in this booklet)

#### Methods - chair Richard Martin

- 14:30 to 15:00 - **Ralph Gebauer**  
A new approach to the correlated many-electron problem
- 15:00 to 15:30 - **Roi Baer**  
Self-averaging stochastic kohn-sham density functional theory, and other acronyms (mp2, rpa, gw,...)
- 15:30 to 16:00 - **Rei Sakuma**  
Systematic construction of symmetry-adapted wannier functions within the maximally-localized wannier function formalism

- 16:00 to 16:30 - Coffee Break

### **Anharmonicity - chair Shobhana Narasimhan**

- 16:30 to 17:00 - **Ion Errea**  
Anharmonic effects from the stochastic self-consistent harmonic approximation: the inverse isotope effect in palladium hydrides
- 17:00 to 17:30 - **Bartomeu Monserrat**  
Anharmonic vibrational properties of solids: theory and applications

### **Poster session - food and wine**

- 18:00 to 20:00 - Poster Session and Buffet Dinner

## **Day 2 - January, 10 2014**

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### **Correlated electrons - chair Eric Koch**

- 9:30 to 10:00 - **Karsten Held**  
electronic correlations beyond dynamical mean field theory
- 10:00 to 10:30 - **Jaejun Yu**  
Physics of  $j=1/2$  electronic state in 5d ir-oxides: topological insulators and quantum magnets
- 10:30 to 11:00 - Coffee Break

### **Low-dimensional materials - chair Alfredo Pasquarello**

- 11:00 to 11:30 - **Steven G. Louie**  
Novel quantum behaviors in atomically thin two-dimensional materials
- 11:30 to 12:00 - **Mey-Yin Chou**  
Physics of few-layer graphene: from neutrino-like oscillations to hofstadter butterflies
- 12:00 to 12:30 - **Michael Rohlfing**  
Optical spectra of carbon nanotubes: defects, stokes shifts, and environment polarizability
- 12:30 to 14:30 - Lunch (on your own – see map of EPFL cafeterias in this booklet)

### **Fundamentals of dft - chair Stefano de Gironcoli**

- 14:30 to 15:00 - **Leeor Kronik**  
The derivative discontinuity – origins, hiding places, and ways to fight it
- 15:00 to 15:30 - **Paula Mori-Sanchez**  
The derivative discontinuity of the exchange-correlation functional

- 15:30 to 16:00 - **Maria Hellgren**  
Molecular dissociation and time-dependent exact-exchange theory

- 16:00 to 16:30 - Coffee Break

### **Novel materials - chair Matteo Cococcioni**

- 16:30 to 17:00 - **Teodoro Laino**  
Screening electrolyte materials for li/air batteries
- 17:00 to 17:30 - **Carlo Antonio Pignedoli**  
Dft challenges following synthesis routes for atomically precise graphene based heterostructures

**Free evening – see suggestions for restaurants at the end of this booklet**

### **Day 3 - January, 11 2014**

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### **Complex electrostatic environments - chair Ursula Roethlisberger**

- 9:30 to 10:00 - **Patrick Rinke**  
Space-charge transfer in hybrid inorganic-organic systems
- 10:00 to 10:30 - **Oliviero Andreussi**  
Adding a continuum to electronic structure calculations
- 10:30 to 11:00 - Coffee Break

### **Exploring phase space - chair Wanda Andreoni**

- 11:00 to 11:30 - **Michele Parrinello**  
From metadynamics to dynamics
- 11:30 to 12:00 - **Fabio Pietrucci**  
Combining graph theory with molecular dynamics: efficient exploration of complex reaction pathways from nanostructures to solutions
- 12:00 to 12:30 - **Maximilian Amsler**  
Ab initio structure prediction with the minima hopping method

### **Closing remarks - Richard Martin**

## 3 Abstracts

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### **Which density functionals work for warm dense hydrogen?**

**David Ceperley**, University of Illinois Urbana-Champaign

Over the past decade [1] we have used Coupled-Electron Ion Monte Carlo to perform equilibrium simulations for systems containing roughly one hundred electrons and protons including quantum effects of both species, making estimates of stable solid phases, transitions between the crystal phases and the liquid, and the transition between competing liquid phases. However, it is desirable to have methods that can treat larger systems, e.g. to calculate dynamical properties such as transport coefficients, to find accurate estimates of critical points or to make a comprehensive survey of a phase diagram. Density Functional Theory can be used for these tasks, however, there are many functionals available today and results can vary. Dense hydrogen places special demands on accuracy since the metallic-insulator transition and the atomic-molecular transition are known to be problematic for DFT. Recently[2], we have assessed accuracy of several functionals by tabulating Quantum Monte Carlo energies and forces for hundreds of configurations of bulk hydrogen under various thermodynamic conditions such as the low temperature crystal, liquid, etc. Using this database, we rate functionals based on various criteria such as mean squared error, maximum error, etc. Which functional has the least error depends on the density/temperature range and property examined. In the vicinity of the atomic-molecular transition, we find the van der Waals functionals give the least biased total energies. We have also performed similar comparisons with liquid water configurations, as have others[3].

[1] J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, *Rev. Mod. Phys.* 84, 1607 (2012).

[2] R. C. Clay, J. Mcminis, J. M. McMahon, C. Pierleoni, D. M. Ceperley and M. A. Morales, "QMC Benchmark of Exchange-Correlation Functionals for High Pressure Hydrogen" (2013).

[3] J. Gergely, PhD thesis, U. of Illinois (2009); M. A. Morales, J. Gergely, J. McMinis, J. M. McMahon, J. Kim, and D. M. Ceperley, "Quantum Monte Carlo benchmark of exchange-correlation functionals for bulk water" (2014); M. J. Gillan, F. R. Manby, M. D. Towler and D. Alfè, *J. Chem. Phys.* 136, 244105 (2012).

### **Semistochastic quantum monte carlo -- a hybrid of of exact diagonalization and quantum monte carlo methods**

**Cyrus Umrigar**, Cornell University

This talk will first provide an overview of various zero-temperature QMC methods, discuss their advantages and disadvantages, and the nature of the infamous "Sign Problem". Then the recently developed Semistochastic Quantum Monte Carlo method[1], which combines some of the advantages of Exact Diagonalization with those of the FCIQMC[2,3] method, developed by the Alavi group, will be discussed.

[1] F. R. Petruzielo, A. A. Holmes, Hitesh J. Changlani, M. P. Nightingale and C. J. Umrigar, *Phys. Rev. Lett.*, 109, 230201, (2012).

[2] George H Booth, Alex Thom and Ali Alavi, *J. Chem. Phys.*, 131, 054106 (2009).

[3] Deidre Cleland, George H Booth, and Ali Alavi, *J. Chem. Phys.*, 132, 041103 (2010).

### **Dft vs. reality: the error budget**

**Stefaan Cottenier**, Kurt Lejaeghere, Jan Jaeken, Veronique Van Speybroeck

Center for Molecular Modeling & Department of Materials Science and Engineering,  
Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium

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Zwijnaarde, Belgium

When applying DFT as a tool for computational materials design, the question inevitably arises: how large is the error bar on your predictions? It will be shown how we obtain a quantitative answer to that question by addressing error contributions at three different levels: codes and methods [1,2], functionals [1,2], predictors [3].

[1] "Error estimates for solid-state density-functional theory predictions: an overview by means of the ground-state elemental crystals", K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier, *Critical Reviews in Solid State and Materials Sciences* 39, 1-24 (2014) [open access, <http://dx.doi.org/10.1080/10408436.2013.772503>]

[2] <https://molmod.ugent.be/deltacodesdft>

[3] "Ab-initio-based thermal property predictions at a low cost: an error analysis", K. Lejaeghere, J. Jaeken, V. Van Speybroeck and S. Cottenier (submitted)

## **Towards a better error assessment of first-principles methods for electronic and optical properties of solids**

**Gian-Marco Rignanese**, Université Catholique de Louvain

Nowadays, density functional theory (DFT) has become the choice tool for first-principles predictions of structural and ground-state properties of condensed matter systems. However, most semi-local exchange-correlation (XC) energy approximations to DFT (such as LDA or GGA) suffer from a pathological underestimation of the band-gap and the dispersion of the bands (hence the bandwidths) is also often poorly described. In contrast, many-body perturbation theory (MBPT) offers an approach for obtaining quasiparticle (QP) energies which is controlled and amenable to systematic improvement. The resulting electronic properties compare much better with experiment. Unfortunately, the MBPT calculations are computationally very time-consuming. Recently, various hybrid and meta-GGA (MGGA) functionals have been constructed to give good band gaps in solids. The hybrid functionals incorporate a fraction of Hartree-Fock (HF) exchange, whose computation increases the CPU time compared to the semi-local counterparts (though it remains shorter compared to MBPT). Furthermore, their reliability has recently been questioned [1] The MGGA functionals use the Laplacian of the density or the kinetic energy density in addition to the density (used in the LDA) and the magnitude of the gradient of the density (used in the GGA). MGGA is, likewise LDA and GGA, a semi-local approximation and, as such, it does not induce a significant increase of the CPU time. However, the mechanism of this improvement is still unclear; and the effectiveness of MGGA functionals for properties other than the band gap itself is still debated [2]. In this talk, I will compare these different formalisms for a variety of systems ranging from metallic alloys to amorphous oxides. I will emphasize that it is not obvious to determine a systematic method to obtain an accurate description of the electronic structure that could be used in a high-throughput framework.

[1] M. Jain, J.R. Chelikowsky, and S.G. Louie, *Phys. Rev. Lett.* 107, 216806 (2011).

[2] D. Waroquier et al., *Phys. Rev. B* 87, 075121 (2013).

## **High-throughput computations as an accelerator for materials discovery: an application to p-type transparent conducting oxides**

**Geoffroy Hautier**, Université Catholique de Louvain

Many essential materials properties can nowadays be computed through ab initio methods. When coupled with the exponential rise in computational power available to research groups, this predictive power provides the opportunity for large-scale computational searches for new

materials. Thousands of materials can be screened by their computed properties even before their full experimental analysis, focusing experiments on the most promising candidates and rapidly exploring new chemical spaces. This new paradigm will be illustrated by the results of a recent large scale search for new low hole effective mass p-type transparent conducting oxides (TCOs). Transparent conducting oxides are essential to many technologies from solar cell to transparent electronics. While n-type TCOs (using electrons as carriers) are widespread in current applications (e.g., indium tin oxides or ITO), their p-type counterparts have been much more challenging to develop and still exhibit carrier mobilities an order of magnitude lower. One of the barriers to the development of high mobility p-type TCOs is the intrinsically high effective masses of holes in oxides. In this talk, I will report on a high-throughput computational search for oxides with low hole effective mass and wide band gap. Screening thousands of binary and ternary oxides using state of the art ab initio techniques, I will present several unsuspected compounds with promising electronic structures. Beyond the description of those novel TCO candidates, I will discuss and chemically rationalize our findings, highlighting several design strategies towards the development of future high mobility p-type TCOs.

### ***A new approach to the correlated many-electron problem***

**Ralph Gebauer**[1], Morrel Cohen [2], Roberto Car[3]

[1] ICTP, Trieste, Italy

[2] Rutgers University, Piscataway, USA

[3] Princeton University, USA

The ground-state energy of a system of many interacting electrons is a key quantity in chemistry and condensed matter physics. In principle, it can be exactly obtained from the many-body wavefunction, but this approach is computationally complex and tractable only in very small systems. For this reason, approximate methods like Hartree-Fock or density-functional theory are playing an important role in numerical approaches to complex systems. Such reduced complexity theories have enabled the study of many kinds of materials and properties with high precision, but many limitations remain. In particular, a correct yet numerically efficient treatment of strong as well as dynamical correlation remains a challenge. In this presentation, I will explain a recently developed approach to this problem. The energy is formulated as a functional in which the basic variables are the natural orbitals and their occupation numbers plus their joint occupation probabilities (OP). The latter are properties of the two-particle density matrix, and the new approach therefore goes beyond well established single-particle reduced density matrix functional theory. Some results for small diatomic molecules and linear chains of hydrogen atoms (up to H<sub>16</sub>) will be presented. From these examples it can be seen that the new approach, which scales like Hartree-Fock, is powerful also at high correlation, i.e. at intermediate and large interatomic separations where Hartree-Fock and other single-reference methods fail due to the multi-reference character of the ground-state wavefunction.

<http://arxiv.org/abs/1309.3929>

### ***Self-averaging stochastic kohn-sham density functional theory, and other acronyms (mp2, rpa, gw,...)***

**Roi Baer**, Eran Rabani, Daniel Neuhauser

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Department of Chemistry and Biochemistry, University of California, Los Angeles,



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We formulate the Kohn-Sham density functional theory (KS-DFT) as a statistical theory in which the electron density is determined from an average of correlated stochastic densities in a trace formula. The key idea is that it is sufficient to converge the total energy per electron to within a predefined statistical error in order to obtain reliable estimates of the electronic band structure, the forces on nuclei, the density and its moments, etc. The fluctuations in the total energy per electron are guaranteed to decay to zero as the system size increases. This facilitates "self-averaging" which leads to sublinear scaling KS-DFT electronic structure. The approach sidesteps calculation of the density matrix and thus is insensitive to its evasive sparseness, as demonstrated here for silicon nanocrystals. The formalism is not only appealing in terms of its promise to far push the limits of application of KS-DFT, but also represents a cognitive change in the way we think of electronic structure calculations as this stochastic theory seamlessly converges to the thermodynamic limit. The methods can be extended to reduce the calculation burden for methods such as MP2, RPA and GW.

- (1) R. Baer D. Neuhauser and E. Rabani, *Phys. Rev. Lett.* 111, 106402 (2013)
- (2) D. Neuhauser, E. Rabani, and R. Baer, *J. Phys. Chem. Lett.* 4, 1172 (2013).
- (3) R. Baer and E. Rabani, *Nano Lett.* 12, 2123 (2012)
- (4) R. Baer and D. Neuhauser, *J. Chem. Phys.* 137, 051103 (2012).
- (5) D. Neuhauser, E. Rabani, and R. Baer, *J. Chem. Theor. Comp* 9, 24 (2012).

### ***Systematic construction of symmetry-adapted wannier functions within the maximally-localized wannier function formalism***

**Rei Sakuma**, Department of Physics, Division Mathematical Physics, Lund University

The maximally-localized Wannier function formalism is a noble approach to construct localized orthonormal set of Wannier functions through the minimization of the so-called spread functional, which describes the spatial spreads of Wannier functions and is closely related to the phase factors of Bloch functions. This formalism, however, does not contain a mechanism to control symmetry properties and centers of Wannier functions, therefore it is sometimes difficult to analyze properties of the calculated Wannier functions. In this talk I present simple addition to this formalism, which allows one to construct Wannier functions having specified symmetries and centers. In this new approach, the minimization of the spread functional is carried out with symmetry constraints derived from the theory of site-symmetry group which depend on user-specified symmetries and centers, therefore one can obtain symmetry-adapted Wannier functions which are not necessarily stable in the original approach. I demonstrate the new approach with some simple examples, and discuss the connection between the symmetries of Wannier functions and the band-structure.

- [1] N. Marzari and D. Vanderbilt, *Phys. Rev. B* 56, 12847 (1997).
- [2] I. Souza, N. Marzari, and D. Vanderbilt, *Phys. Rev. B* 65, 035109 (2001).
- [3] R. Sakuma, *Phys. Rev. B* 87, 235109 (2013).

### ***Anharmonic effects from the stochastic self-consistent harmonic approximation: the inverse isotope effect in palladium hydrides***

**Ion Errea**[1,2,3], Matteo Calandra [1] and Francesco Mauri [1]

- [1] Universite Pierre et Marie Curie (UPMC), CNRS, IMPMC, Paris, France
- [2] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain
- [3] Donostia International Physics Center (DIPC), San Sebastian, Spain

Describing vibrations of atoms is of paramount importance in the physical properties of solids. Nowadays, phonon dispersions in the harmonic approximation are routinely calculated from

first-principles. Nevertheless, whenever the displacements of the atoms largely exceed the range in which the harmonic potential is valid, the harmonic approximation completely fails, as well as any perturbative approach based on it. Here we present a newly developed approach to treat strongly anharmonic systems valid at any temperature: the stochastic self-consistent harmonic approximation (SSCHA). The SSCHA is based on the minimization of the free energy with respect to a trial density matrix described by an arbitrary harmonic Hamiltonian. The minimization is performed with respect to all the free parameters in the trial harmonic Hamiltonian, namely, equilibrium positions, phonon frequencies and polarization vectors. The gradient of the free energy is calculated following a stochastic procedure. The method can be used to calculate thermodynamic properties, dynamical properties and even anharmonic corrections to the Eliashberg function of the electron-phonon coupling. We demonstrate the validity of the method applying it to palladium hydrides. Superconducting palladium hydrides display the largest isotope effect anomaly known in literature since replacement of hydrogen with the heavier isotopes leads to higher superconducting temperatures, a behavior inconsistent with harmonic theory. We show that the large isotope anomaly is entirely due to the huge anharmonicity of hydrogen rattling modes.

[1] Ion Errea, Matteo Calandra, and Francesco Mauri, *Phys. Rev. Lett.* 111, 177002 (2013).

[2] Ion Errea, Matteo Calandra, and Francesco Mauri, *arXiv:1311.3083 [cond-mat.mtrl-sci]*.

## **Anharmonic vibrational properties of solids: theory and applications**

**Bartomeu Monserrat**[1], N.D. Drummond [2], R.J. Needs [1]

[1] University of Cambridge, United Kingdom

[2] Lancaster University, United Kingdom

The harmonic approximation to the vibrational motion of nuclei in solids is an excellent approach in the vast majority of systems. However, anharmonic terms could be important in a range of situations such as in systems with light nuclei or at high temperatures, or systems with harmonic instabilities that are stabilized by temperature. We will describe an approach for the calculation of the anharmonic vibrational energy of solids [1] that is based in sampling the Born-Oppenheimer energy surface beyond the harmonic terms, and solving the resulting vibrational equation within a mean-field formalism. We will also discuss how the scheme can be extended to evaluate the coupling between the vibrational state of a system and a general physical quantity, and we will focus on the temperature dependence of the electronic band gap in semiconductors and insulators. We will exemplify the methodology by considering two applications: (i) the dissociation of high-pressure solid hydrogen [2], and (ii) the metallization of solid helium at terapascal pressures [3]. In the first, we use quantum Monte Carlo and anharmonic vibrations to determine a new dissociation pressure of 370 GPa, significantly lower than previous estimates and close to experimentally available pressures. In the second, we calculate the pressure-temperature phase diagram of solid helium including the effects of electron-phonon coupling on the band gap, and find a metallization pressure higher than previously believed. Our results have implications for the cooling of white dwarf stars.

[1] B. Monserrat, N.D. Drummond, and R.J. Needs, "Anharmonic vibrational properties in periodic systems: energy, electron-phonon coupling, and stress" *Phys. Rev. B* 87, 144302 (2013).

[2] S. Azadi, B. Monserrat, W.M.C. Foulkes, and R.J. Needs, "Dissociation of high-pressure solid molecular hydrogen: a quantum Monte Carlo and anharmonic vibrational study" (2013).

[3] B. Monserrat, N.D. Drummond, C.J. Pickard, and R.J. Needs, "Electron-phonon coupling and the metalization of solid helium at terapascal pressures" *arXiv:1311.1005 [cond-mat.mtrl-sci]* (2013).

## **Electronic correlations beyond dynamical mean field theory**

**Karsten Held**, TU Wien

Dynamical mean field theory (DMFT) has been a big step forward for our understanding of

electronic correlations. A major part of the electronic correlations, the local ones, are included. On the other hand, DMFT neglects non-local correlations that are at the origin of many physical phenomena such as (quantum) criticality, high-T superconductivity, weak localization and other vertex corrections to transport in nanoscopic systems. To address these topics the scientific frontier moved to cluster and diagrammatic extensions of DMFT such as the dynamical vertex approximation [1]. I will present an introduction to the diagrammatic extensions of DMFT and discuss selected applications such as the calculation of critical exponents [2].

[1] A. Toschi, A. A. Katanin, and K. Held, *Phys. Rev. B* 75, 045118 (2007); A. N. Rubtsov, M. I. Katsnelson, and A. I. Lichtenstein, *Phys. Rev. B* 77, 033101 (2008); G. Rohringer, A. Toschi, H. Hafermann, K. Held, V.I. Anisimov, and A. A. Katanin, *Phys. Rev. B* 88, 115112 (2013); C. Taranto, S. Andergassen, J. Bauer, K. Held, A. Katanin, W. Metzner, G. Rohringer, A. Toschi, *arXiv:1307.3475*.

[2] G. Rohringer, A. Toschi, A. Katanin, and K. Held, *Phys. Rev. Lett.* 107, 256402 (2011).

## **Physics of $j=1/2$ electronic state in 5d ir-oxides: topological insulators and quantum magnets**

Jaejun Yu, Seoul National University, Seoul, Korea

Since the  $J=1/2$  state was first reported in Ir oxides [1] as a unique manifestation of the spin-orbit coupling (SOC) and on-site Coulomb interaction effect, there has been an enormous interest in 5d transition metal oxides as a candidate for exotic topological insulators and quantum magnet materials. In this talk we will discuss the role of electron correlation combined with strong SOC under a large crystal field, which is responsible for the observed  $J=1/2$  state, and further an interesting competition between local lattice distortion and spin-orbit coupling, which controls the degree of  $J=1/2$  components near the Fermi level. We investigate a possible topological quantum phase transition driven by the control of long-range hopping and trigonal crystal field [2]. In addition, we observe that intriguing effective magnetic interactions arise from the strong spin-orbit coupling with on-site Coulomb interaction. Possible topological insulator and exotic magnetic phases suggest that Ir-oxide and related systems can be an "interesting" playground for the study of the interplay between spin-orbit coupling and on-site Coulomb interaction.

[1] B. J. Kim et al., *Phys. Rev. Lett.* 101, 076402 (2008).

[2] C. H. Kim et al., *Phys. Rev. Lett.* 108, 106401 (2012).

## **Novel quantum behaviors in atomically thin two-dimensional materials**

Steven G. Louie, University of California at Berkeley and Lawrence Berkeley National Laboratory, USA

Recent experimental and theoretical studies of atomically thin two-dimensional materials have revealed that these systems can exhibit highly unexpected behaviors. In this talk, we discuss theoretical predictions of novel quantum behaviors in two such systems. 1) We show that monolayer transition metal dichalcogenides (such as MoS<sub>2</sub>) possess a large and diverse number of strongly bound excitonic states with novel k-space characteristics not previously seen experimentally or theoretically. Interesting two-photon and intra-exciton absorption phenomena are predicted. 2) We discover that electron supercollimation can be achieved in graphene or other 2D Dirac fermion systems by using one-dimensional disorder potentials. An electron wave packet is guided to propagate undistorted along the fluctuating direction of the external disorder potential, independent of its initial motion.

## **Physics of few-layer graphene: from neutrino-like oscillations to hofstadter butterflies**

**Mey-Yin Chou**, School of Physics, Georgia Institute of Technology, Atlanta, Georgia, USA, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

It has become possible in recent years to fabricate and manipulate two-dimensional (2D) nanomaterials in the laboratory that are as thin as one to few atomic layers. A well-known example is graphene, where the Dirac-Weyl Hamiltonian for massless fermions describes the low-energy quasiparticles. Intriguing physics has been found in these few-layer systems, and phenomena originally associated with particle physics can now be observed in condensed matter systems. In this talk, I will focus on our recent computational studies of a few representative systems, including the neutrino-like oscillation and anisotropic transport [1] in twisted bilayer graphene that also exhibits a rare fractal-like “butterfly” energy spectrum under external magnetic field [2]. In addition, I will also discuss the possibility of growing 2D structures of other group-IV elements on graphene. It is expected that many of the unique electronic properties of graphene can also be realized in this new 2D system. We have performed first-principles calculations of silicene on graphene [3] in order to understand the effect of substrate interaction on the physical properties of these systems. The phonon properties and electron-phonon interaction of freestanding silicene [4] will also be discussed. This work is in collaboration with Lede Xian, Zhengfei Wang, Chih-Piao Chuu, Yongmao Cai, Jia-An Yan, and Ching-Ming Wei.

[1] L. Xian, Z. F. Wang, and M. Y. Chou, *Nano Lett.* 13, 5159 (2013).

[2] Z. F. Wang, F. Liu, and M. Y. Chou, *Nano Lett.* 12, 3833 (2012).

[3] Y. Cai, C.-P. Chuu, C. M. Wei, and M. Y. Chou, *Phys. Rev. B* 88, 245408 (2013).

[4] J.-A. Yan, R. Stein, D. M. Schaefer, X.-Q. Wang, and M. Y. Chou, *Phys. Rev. B (Rapid Communications)* 88, 121403 (2013).

### ***Optical spectra of carbon nanotubes: defects, stokes shifts, and environment polarizability***

**Michael Rohlfing**, University of Muenster, Institute for Solid-State Theory, Germany

The optical spectrum of a semiconducting carbon nanotube (CNT) is dominated by excitonic states. The excitons of a perfect CNT can be modified significantly by internal structural defects, as well as by its environment, often resulting in redshifts of characteristic spectral lines. Such effects can be described by ab-initio many-body perturbation theory, in particular by the GW self-energy operator in combination with the Bethe-Salpeter equation (GW-BSE). Here we discuss the influence of oxygen and hydrogen adatoms, accompanied by Stokes shifts due to structural relaxation [1], as well as redshifts from the environment polarizability of neighboring CNT and of physisorbed gas molecules [2]. The latter effects are subtle and tiny and require a simplified, perturbative realization of GW-BSE [3].

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### ***The derivative discontinuity – origins, hiding places, and ways to fight it***

**Leeor Kronik**, Weizmann Institute of Science, Rehovoth 76100, Israel

The derivative discontinuity (DD) [1] is an important quantity within Kohn-Sham density functional theory (DFT), which has often generated confusion. Briefly, it is a singularity in the Kohn-Sham map, wherein as the number of electrons crosses an integer, the exchange-correlation (xc) potential may “jump” by a constant. This constant, believed to be missing from standard xc approximations, has severe implications, as it suggests that fundamental gaps cannot be captured from DFT frontier orbital energies even in principle. In this talk, I will clarify

some properties of the DD, dispel some myths surrounding it, and suggest strategies for overcoming the gap problem. In particular, I will show that: 1. The DD can have clear footprints even in the ground-state xc potential [2]. 2. Every approximate xc functional has an easily quantifiable DD, even those that are “not supposed to” possess it, if ensemble-DFT arguments are used [3]. It can be used to improve gap predictions. 3. If ensemble-DFT is ignored (which is the standard procedure), xc functionals develop “curvature” at fractional electron numbers. This quantitatively compensates for the missing DD and can be used to extract it [4]. 4. Even “hybrid” functionals, belonging in the generalized Kohn-Sham family, can possess a DD [4,5]. 5. Last but not far from least: Range-separated hybrid functionals can be constructed from first principles so as to explicitly minimize the DD. They accurately capture fundamental gaps in molecules [5,6] and provide a quantitatively useful approximation for outer valence states excitation energies [7].

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## ***The derivative discontinuity of the exchange-correlation functional***

**Paula Mori-Sanchez**[1], Aron J Cohen [2]

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The derivative discontinuity is a fundamental feature of the exchange-correlation energy. It is the change in the derivative of the energy as the number of electrons goes through an integer, and it is often expressed as a potential that jumps by a constant on going from  $N\hat{+}^{\hat{+}}$  to  $N\hat{+}^{\hat{+}}$ . In this talk we will show manifestations in the total energy of integer systems at fixed  $N$ . One manifestation is the complete failure of all functionals in the literature to give the energy of both infinitely stretched  $H_2^+$  and infinitely stretched  $H_2$ . Another very clear example is the failure to correctly reproduce the density in a two electron  $H_2$  like system when changing the charge of one of the protons to be non-integer. More examples in chemistry and physics will be shown, ranging from the behaviour of electrons in the simplest chemical reactions to the gap of the 1D-Hubbard model and electron transport in the Anderson model. To understand the derivative discontinuity in these systems it is important to consider three perspectives, (1) the true behaviour of electrons which can be found by an exact FCI calculation (2) the failures of most currently used approximate functionals, which are all missing the derivative discontinuity (3) investigating new functionals that may have some aspects of the derivative discontinuity. This is a great challenge for  $Exc[\hat{+}]$  and critical for the description of phenomena such as metal-insulator transitions, which will be illustrated by another simple model system.

## ***Molecular dissociation and time-dependent exact-exchange theory***

**Maria Hellgren**, International School for Advanced Studies (SISSA), Trieste

The adiabatic connection fluctuation dissipation (ACFD) formula is an exact expression for the correlation energy in terms of the dynamical density-density response function. The first level of approximation is the random phase approximation (RPA) which already incorporates many important features known to be difficult to capture with standard correlation functionals. For example, it contains the weak van der Waals forces, and the problem of large static correlation errors which appear in the dissociation limit of molecules are almost entirely absent within the RPA. However, many properties are in quantitative error with experiment and certain features of

strong electron correlation are missing. In this talk I will show how the inclusion of exchange effects in the response function yields correlation energies, van der Waals coefficients and molecular dissociation energies in excellent agreement with experimental values. Special attention will be given to the dissociation of molecules with open-shell fragments and how to predict the dissociation limit in terms of a so-called fractional charge analysis.

## **Screening electrolyte materials for li/air batteries**

**Teodoro Laino**, Katharina Meyer, Alessandro Curioni, IBM Research Zurich GmbH

Lithium-air batteries have captured worldwide attention because, theoretically, their specific energy far exceeds the best achieved with modern battery solutions, allowing an electric vehicle to run for mileage ranges similar to the ones of gasoline vehicles. However, lithium/air batteries, still present significant challenges, mostly related to materials. In this talk, I will review the status and computational materials challenges for non-aqueous lithium/air electrochemical cells with particular attention to (1) the chemical stability of different candidate solvents versus lithium peroxide and (2) to the understanding of novel lithium-ion conducting ceramics.

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## **DFT challenges following synthesis routes for atomically precise graphene based heterostructures**

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3 Max Planck Institut for Polymer Research, Mainz

The application of graphene in microelectronics is, in principle, hampered by the absence of a band gap in its electronic structure. Cutting grapheme into nanometre-wide ribbons, termed graphene nano ribbons (GNRs) allows to introduce a band gap in its electronic structure. GNRs are promising building blocks t for the fabrication of novel electronic devices [1] however, standard fabrication techniques, based on top-down approaches for cutting graphene or carbon nanotubes into GNR like structures, are not suitable for ribbons narrower than  $\sim 5$  nm. A bottom-up approach based on surface-assisted cyclodehydrogenation reactions proposed recently by EMPA has emerged as a promising route to the synthesis of nanoribbons and nanographenes [2, 3]. The key step of this bottom-up GNR fabrication method is the thermally induced cyclodehydrogenation of linear polyphenylenes on noble-metal templates (see Figure 1). I will discuss the successes and limitations of DFT based atomistic simulations in understanding/driving experiments for our most recent results in the synthesis [4] and characterisation [5,6] of atomically precise GNR based heterostructures.

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## **Space-charge transfer in hybrid inorganic-organic systems**

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

The properties of hybrid inorganic/organic systems (HIOS) can be tuned by inserting dipolar layers at the interface between the two materials. To study the interface between ZnO and molecular dipole layers we use quantum mechanical first-principles approaches. To take the bulk doping concentration of ZnO into account, I here present an approach that introduces excess charge in the unit cell by means of the virtual crystal approximation with fractionally charged nuclei [1] and that includes the energy contribution of space-charge layers and the associated band bending explicitly [1-3]. For the bulk terminated ZnO(000-1) surface covered with half a monolayer of hydrogen (2x1-H), I demonstrate that electrons from bulk dopants can stabilize deviations from this half monolayer coverage at low hydrogen pressures [2]. Ambient hydrogen background pressures are therefore more conducive than ultra high vacuum conditions to form the defect free, semiconducting 2x1-H surface, which would be a more controlled substrate in HIOS [2]. For the interface between ZnO(000-1) 2x1-H and tetrafluoro-tetracyanoquinodimethane (F4TCNQ) monolayers, I show that the adsorption energy and the charge transfer to the molecules depend strongly on the bulk dopant concentration. While the build-up of a space-charge layer is not unexpected, the magnitude of its effect is astounding: the adsorption energy of F4TCNQ changes by more than 2~eV and more than doubles from low to high doping [3]. In the limit of low bulk doping concentrations, charge transfer becomes vanishingly small in agreement with photoemission data [3], while the F4TCNQ induced work function increase remains unaffected and large. The bulk doping concentration and the associated build-up of a space-charge layer therefore provide an additional way to tune the interface properties in HIOS and might generally affect interface properties.

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## **Adding a continuum to electronic structure calculations**

**Oliviero Andreussi**, University of Pisa, Pisa, Italy

Acquiring a real predictive power in materials modeling requires increasing the complexity and realism of simulated systems. While fully atomistic approaches may sometimes be viable, more advanced strategies are required in order to keep the high-throughput capabilities of ab-initio methods. Continuum models represent an invaluable tool for a multiscale description of complex environments in electronic structure calculations. In this talk, two complementary approaches are presented, which extend the use of continuum models beyond the usual study of solvation effects in isolated systems. First, some recent developments in the theory and implementation of continuum models will be presented, showing how a fully variational, self-consistent continuum solvation (SCCS) model [1], defined on a much reduced number of parameters, can be effectively included in plane-wave electronic structure codes. The resulting method is perfectly suited for simulations of periodic systems and for ab-initio molecular dynamics simulations. Applications of SCCS to neutral [1] and charged [2] compounds are presented, together with its on-going extensions to the study of electrochemical systems and to the modeling of electronic excitations in solution. Second, continuum models can be extended beyond the field of classic solvation effects: they can be used, for example, to couple the complex dielectric response of plasmonic nanoparticles to the electronic properties of organic chromophores [3], thus allowing the characterization of plasmon-enhanced optical properties of atomistic systems, treated with full details. By combining continuum models with a polarizable QM/MM approach, the resulting multiscale approach can be used to study bio-hybrid devices, in which metal nanoparticles are used to enhance the light-harvesting properties of photosynthetic

proteins [4].

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## ***From metadynamics to dynamics***

**Michele Parrinello**, Department of Chemistry and Applied Biosciences, ETH, 8092 Zurich, Switzerland and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera Italiana, Via Giuseppe Buffi 13, 6900 Lugano, Switzerland

Metadynamics is a commonly used and successful enhanced sampling method. By the introduction of a history dependent bias which depends on a restricted number of collective variables it can explore complex free energy surfaces characterized by several metastable states separated by large free energy barriers. Here we extend its scope by introducing a simple yet powerful method for calculating the rates of transition between different metastable states. The method does not rely on a previous knowledge of the transition states or reaction coordinates, as long as collective variables are known that can distinguish between the various stable minima in free energy space. We demonstrate that our method recovers the correct escape rates out of these stable states and also preserves the correct sequence of state-to-state transitions, with minimal extra computational effort needed over ordinary metadynamics. We apply the formalism to three different problems and in each case find excellent agreement with the results of long unbiased molecular dynamics runs.

## ***Combining graph theory with molecular dynamics: efficient exploration of complex reaction pathways from nanostructures to solutions***

**Fabio Pietrucci**, Wanda Andreoni, Gregoire Gallet, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

Viewing a molecule or a condensed matter system as a network of chemical bonds allows to employ in computational physics a number of powerful tools borrowed from graph theory. Traditionally, this has been exploited in databases correlating static molecular geometries with useful physico-chemical properties. I will present a different point of view, where graph theory is exploited in combination with molecular dynamics and enhanced sampling techniques, allowing to discover complex multi-step reaction pathways. At the core of the methodology lies the development of new topological coordinates derived from the adjacency matrix of chemical bonds and invariant upon permutation of identical atoms [1,2]. I will illustrate two problems that can be tackled in a fresh new way by means of our approaches: complex transformations of nanostructures [1,3] and chemical reactions in water solution [2].

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## ***Ab initio structure prediction with the minima hopping method***

**Maximilian Amsler**, Stefan Goedecker, Basel University, Switzerland

Due to increased computational power and development of new methods, theoretical structure prediction based on density functional theory has become a popular method to predict new materials and to help in the interpretation of experimental measurements. The minima hopping



method is a simple but powerful tool to find low energy structures of a system given only its chemical composition. It exploits basic physical principles and its range of applications has constantly been extended in recent years. Currently, it can be used for structure prediction of clusters, biomolecules, surfaces and crystals. I will present the results of our studies on carbon and boron fullerenes, on the reconstruction of boron surfaces and on crystalline compounds where novel phases of various hydrogen storage materials were found.

## 4 Posters

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### **Electronic structure of the giant Rashba splitting semiconductor BiTeI**

**Gabriel Autes**[1], O. V. Yazyev  
ITP, EPFL, Lausanne, Switzerland

BiTeI is a layered semiconductor that lacks inversion symmetry and features strong spin-orbit coupling responsible for a giant Rashba spin splitting of both bulk and surface states [1,2]. The surface of this material has two distinct terminations characterized by p- and n-type conduction [2], which makes BiTeI a promising candidate for spintronics applications. We present a first-principles study of the structural and electronic properties of bulk BiTeI and its surfaces. In particular, we find record values of the Rashba splitting of the surface states in agreement with recent experiments [2]. The properties of boundaries between domains with different surface terminations are also investigated. Finally, we discuss the possibility for a pressure-induced topological phase transition in this material. It was predicted that pressure lead to gap closure with further reopening resulting in a strong  $Z_2$  topological insulator type band structure [3]. Using the GW approximation calculations we show that the predicted topological phase transition is hindered by the structural phase transition taking place at a lower pressure [4,5].

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### **Controlling magnetism on metal surfaces with electric field and surface charging**

**Tamene Regassa Dasa**[1], Oleg O. Brovko[1], Pedro Ruiz-Díaz[1], Valeri S. Stepanyuk[1]  
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Magnetoelectric coupling based on the manipulation of charge carriers has proven to be a promising mechanism of tuning exchange interaction between atomic adsorbates or the magnetic anisotropies of atomic chains and alloy multilayers. [1-5] In these studies prospective ways of controlling charge carriers (charge doping or application of external electric field) are outlined. Based on our ab-initio studies we show clear evidences that either surface-charging or external electric fields (EEF) might be used to tailor the magnetic anisotropy (MA) or exchange coupling of layered systems. [3,4] We consider 3d-5d metal alloys which are known to have large perpendicular magnetic anisotropy. Further, it is pointed out that the MA or interlayer exchange coupling of alloy multilayers can be strongly tuned by surface-interface charging. Remarkably, a modest amount of charge injection can switch the easy-axis axis of magnetization of ultra-thin films or the interlayer magnetic order. [3] Moreover, we discuss the possibility to influence the quantum well states in metallic multilayers with EEF and thereby the magnetic anisotropy.[4] By analyzing the variation in the electronic structure of the constituent layers, the local changes in the magnetic properties can be explained.

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### ***Thermal conductivity of graphene from first principles***

**Andrea Cepellotti**[1], Giorgia Fugallo [2], Lorenzo Paulatto [3], Nicola Bonini [4], Michele Lazzeri [3], Francesco Mauri [3], and Nicola Marzari [1]

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We compute the thermal conductivity of graphene by solving the Boltzmann Transport Equation (BTE) for phonons [1], with the phonon-phonon collision rates obtained from density-functional perturbation theory. We find that in graphene the single-mode relaxation time approximation (SMRTA) cannot describe heat transport correctly, underestimating by at least one order of magnitude the thermal conductivity and phonons' mean free paths. Instead, we show that the exact self-consistent solution of the BTE provides results in excellent agreement with experimental measurements [2]. The shortcomings of the SMRTA lie in the assumption that heat flow is transferred only by individual phonon excitations, whereas in layered materials the transport can only be explained in terms of collective phonon excitations. The characteristic length of these collective excitations is often comparable with that of the experimental sample - as a result, even Fourier's law become questionable, since its statistical nature makes it applicable only to systems larger than a few mean free paths.

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### ***QMC molecular dynamics for dense liquid hydrogen***

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Hydrogen is the simplest element in nature and nevertheless its phase diagram at high pressures remains a challenge both from the experimental and theoretical point of view [1]. Here we report the first large scale Quantum Monte Carlo - molecular dynamics (QMC-MD) simulations on dense liquid hydrogen. By means of a novel Langevin MD scheme [2] we can deal with QMC noisy forces and obtain long and equilibrated simulations even for large number of electrons. We find that the molecular liquid phase is unexpectedly stable and the transition towards a fully atomic liquid phase occurs at much higher pressure than previously believed [3]. The old standing problem of low temperature atomization is, therefore, still far from experimental reach.

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### ***Correlation energy from adiabatic connection fluctuation-dissipation theorem including exact exchange kernel***

**Nicola Colonna**[1], Stefano de Gironcoli [1,2]

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We have developed an expression for the electronic correlation energy via the Adiabatic Connection Fluctuation-Dissipation Theorem[1,2] (ACFDT) going beyond the Random-Phase Approximation (RPA) by including exact exchange contribution to the kernel[3,4] (RPax). Our derivation is valid and efficient for general systems. It is based on an eigenvalue decomposition of the time dependent response function[5] of the Many Body system in the limit of vanishing coupling constant, evaluated by Density Functional Perturbation Theory. We tested the accuracy of this approximation on the homogeneous electron gas. Within RPax, the correlation energy of

the homogeneous electron gas improves significantly with respect to the RPA results up to densities of the order of  $r_s^{-1} \approx 10$ . However, beyond this value, the RPax response function becomes pathological and the approximation breaks down. We have also evaluated the dependence of the correlation energy on the spin magnetization of the system. Both RPA and RPax are in excellent agreement with accurate Quantum Monte Carlo results. Moving to non-homogeneous system, we calculated the RPax dissociation curve of weakly interacting dimers. Close to equilibrium distance RPax works better than simple RPA while for large inter-atomic distances the good performance of RPA is maintained.

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### **High magnetization density in Fe and Fe nitrides**

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[2] Earth and Life Science Institute, Tokyo Institute of Technology, Japan

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The ordered Fe nitride Fe<sub>16</sub>N<sub>2</sub> has long been argued to possess a surprisingly large saturation magnetization whose origin, however, has not yet been completely understood. After a long controversy on the existence of the “super-magnetic” phase, recent experiments have re-sparked the interest on this material with the synthesis of Fe<sub>16</sub>N<sub>2</sub> thin films (on various substrates) that show a saturation magnetization exceeding 3T. In this poster I will present the results of our DFT calculations to investigate the electronic and structural properties of Fe<sub>16</sub>N<sub>2</sub>, both in its bulk phase and strained state with a level of strain mimicking the microscopic structure of thin films. Other Fe-N compounds were also considered. In particular, I will show how the study of Fe<sub>3</sub>N has led to the discovery of a new ferromagnetic phase of bulk Fe, exhibiting the highest magnetization density among all the known allotropes. Characterized by a three-fold modulation of the crystal structure, the new phase can be understood as the ferromagnetic “alter-ego” of the FCC crystal, into which it transforms at sufficiently high pressure, upon suppression of the atomic magnetization.

### **DFT+frontier orbital U**

**Emine Kucukbenli**, Nicola Marzari

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Starting from the proof of Janak's theorem, we trace the causes and consequences of piecewise linearity of total energy with respect to occupations. Piecewise linearity is not only a fundamental property that should be obeyed by any exact energy functional, but also a starting point to improve approximate functionals that are used in practical applications. One such improvement recipe is DFT+Hubbard U formalism, which enforces piecewise linearity on the chosen Hubbard manifold [1], generally chosen as localized d or f orbitals. DFT+U has been shown to greatly improve the accuracy of density functional theory for materials with such localized orbitals, such as transition-metal complexes. It has been demonstrated that the piecewise linearization of DFT+U achieves better accuracy by correcting for self-interaction errors [2]. However, DFT+U still performs poorly in complexes where significant covalency is present, and intersite corrections (so-called DFT+U+V) have been introduced to improve these challenging cases [3]. Here, we revisit the origins of piecewise linearity within the DFT+U and DFT+U+V correction schemes, explore the dependence of correction on the manifold choice, and on the details of the ab initio calculation of U and V parameters. Based on this understanding, we propose an approach where self-interaction corrections are applied directly to the frontier orbitals and we suggest a corresponding numerical recipe to calculate the necessary ab initio parameters. In the case of a small transition metal oxide, MnO molecule, we compare this approach to highly accurate quantum chemistry calculations.

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### ***High-pressure structures of disilane and their superconducting properties***

**José A. Flores Livas**[1], Maximilian Amsler [2], Thomas J. Lenosky [3] Lauri Lehtovaara [1], Silvana Botti [1], Miguel A. L. Marques [1] Stefan Goedecker [2]. [1] Université de Lyon, F-69000 Lyon, France, and LPMCN, CNRS, UMR 5586, Université Lyon 1, F-69622 Villeurbanne, France. Current: Max-Planck-Institut für Mikrostrukturphysik Weinberg 2, D-06120 Halle, Germany. [2] Department of Physics, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland [3] C8 Medisensors, Los Gatos, California 95032, USA.

A systematic ab initio search for low-enthalpy phases of disilane (Si<sub>2</sub>H<sub>6</sub>) at high pressures was performed based on the minima hopping method. We found a novel metallic phase of disilane with Cmcm symmetry, which is enthalpically more favorable than the recently proposed structures of disilane up to 280 GPa, but revealing compositional instability below 190 GPa. The Cmcm phase has a moderate electron-phonon coupling yielding a superconducting transition temperature T<sub>c</sub> of around 20 K at 100 GPa, decreasing to 13 K at 220 GPa. These values are significantly smaller than previously predicted T<sub>c</sub>'s for disilane at equivalent pressure. This shows that similar but different crystalline structures of a material can result in dramatically different T<sub>c</sub>'s and stresses the need for a systematic search for a crystalline ground state.

### ***MP2 energy gradients with resolution-of-identity approximation in the condensed phase: an efficient and massively parallel Gaussian and plane waves approach***

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The canonical second-order Moller-Plesset perturbation energy (MP2) is an increasingly popular post-Kohn-Sham correlation method. It recovers a relatively large part of dynamic correlation and, most notably, it introduces dispersion interactions in a completely non empirical way. 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 energy and analytic gradient of finite and extended systems. The key aspect of the method is that the three center electron repulsion integrals (∫∫∫|K) necessary in the RI approximation are computed by direct integration between the products of Gaussian basis functions ∫∫∫ 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. Moreover, our implementation has low memory requirements and displays excellent parallel scalability up to tens thousands of processes. In this way, RI-MP2 energy gradient calculations for condensed phase systems containing hundreds of atoms and thousands of basis functions can be performed within minutes employing few hundred hybrid nodes. In order to validate the presented method, various molecular crystals and bulk liquid water have been employed as benchmark systems to assess the performance.

### ***First-principles simulation of electron transport in realistically large nanoelectronic devices***

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In light of technological challenges involved in manufacturing nanoscale electronic devices, the development of fast, accurate, and reliable computer-aided design tools with atomistic simulation capabilities is becoming a necessity to accelerate the design of new prototypes and reduce the development cost. Density functional theory (DFT) -based quantum transport approaches can rigorously model electron transport phenomena in nanometer-sized devices while taking into account the material properties of the simulated structure from first-principles. In this context, we aim at developing an efficient massively parallel simulator based on DFT and Non-equilibrium Green's Function (NEGF) methods that can simulate realistically large nanostructures with active regions composed of tens of thousands of atoms. Our approach is coupling the DFT simulation package, CP2K, and the quantum transport simulator, OMEN, and leveraging their respective strengths such accurate and efficient algorithms, high scalability, and wide range of applications.

### ***Defect ordering and defect-domain wall interactions in pbtio3 : a first-principles study***

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The properties of ferroelectric materials, such as lead zirconate titanate (PZT), are heavily influenced by the interaction of defects with domain walls. These defects are either intrinsic, or are induced by the addition of dopants. We study here PbTiO<sub>3</sub> (the end member of a key family of solid solutions) in the presence of acceptor (Fe) and donor (Nb) dopants, and the interactions of the different defects and defect associates with the domain walls. For the case iron acceptors, the calculations point to the formation of defect associates involving an iron substitutional defect and a charged oxygen vacancy. This associate exhibits a strong tendency to align in the direction of the bulk polarization; in fact, ordering of defects is also observed in pure PbTiO<sub>3</sub> in the form of lead-oxygen divacancies. Conversely, calculations on donor-doped PbTiO<sub>3</sub> do not indicate the formation of polar defect complexes involving donor substitutions. Last, it is observed that both isolated defects in donor-doped materials and defect associates in acceptor-doped materials are more stable at 180 degree domain walls. However, polar defect complexes lead to asymmetric potentials at domain walls due to the interaction of the defect polarization with the bulk polarization. The relative pinning characteristics of different defects are then compared, to develop an understanding of defect-domain wall interactions in both doped and pure PbTiO<sub>3</sub>. These results may also help understanding hardening and softening mechanisms in PZT.

### ***Defect energy levels in hybrid density functional and many-body perturbation theory***

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The theoretical characterization of point defects in semiconductors and insulators becomes an indispensable tool to understand and exploit the exotic properties of such defects in electronics and optoelectronics. Defect energy levels calculated within the popular (semi)local density functionals are often considered unreliable as the band gaps are severely underestimated. Various schemes are proposed towards more realistic descriptions of defect levels without the "band-gap problem", including the hybrid density functional incorporating a fraction of Fock exchange [1], and the Green's function method within the more elaborate many-body perturbation theory [2]. In the present work, we investigate the defect energy levels of some localized point defects through the hybrid density functionals (PBE0 and HSE) and the G<sub>0</sub>W<sub>0</sub> approximation.[3] We find that the total-energy difference method using (hybrid) density functionals yields highly compatible defect levels to the G<sub>0</sub>W<sub>0</sub> scheme, provided the electronic structure are aligned with respect to the electrostatic potential. In particular, we address the finite-size effect due to the spurious electrostatic interaction in the periodic boundary condition, and highlight the role of delocalization error and the choice of calculation paths in the determination of defect levels within the G<sub>0</sub>W<sub>0</sub> scheme. Our results substantiate the need of a

correct description of band edges in the study of defect energy levels.

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### **Coupling topological insulators and magnetic materials: a first-principles study**

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Combining topological insulators with magnetic materials reveals a rich variety of novel physical phenomena [1,2,3]. Our first-principles calculations address the properties of magnetic impurities on the surface of topological insulators and interfaces between topological insulators and magnetic materials. In particular, we investigate Fe adatoms on the surface of Bi<sub>2</sub>Te<sub>3</sub> topological insulator in the context of a recent experimental study [4]. Our calculations performed at the LDA+U level of theory reveal preferred adsorption sites, magnetic moments and large magnetic anisotropy energies of Fe adatoms in agreement with experimental results.

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### **Bridging density-functional and many-body perturbation theory: orbital-density dependence in electronic-structure functionals**

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Energy functionals which depend explicitly on the orbital densities (ODD), instead of the total charge density, appear when applying self-interaction corrections to density-functional theory. In these cases (e.g. the Perdew-Zunger [1] and the non-Koopmans [2] approaches) the total energy loses invariance under unitary rotations of the orbitals, and the minimization of the functionals leads to orbital-dependent Hamiltonians. We show that it is possible to identify the orbital-dependency of densities and potentials with an effective and discretized frequency-dependency, in close analogy to the quasi-particle approximation of frequency-dependent self-energies and naturally oriented to interpret electronic spectroscopies [3]. Some of the existing ODD functionals are analyzed from this new perspective. Numerical results for the electronic structure of gas-phase molecules (within the Koopmans-corrected class of functionals) are computed and found in excellent agreement with photoemission (UPS) data [4].

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### **First principles study of interfacial defects at (In)GaAs/oxide interfaces**

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We address defects at the (In)GaAs/oxide interfaces that might give rise to band-gap defect

states and cause Fermi level pinning. Calculations are performed within a hybrid-density-functional scheme which correctly reproduces the semiconductor band gap. In particular, we focus our attention on interfacial As-As dimers and Ga dangling bonds. Their defect states are determined as charge transition levels which are directly comparable with experimental data obtained through current-voltage measurements. We accurately achieve abrupt interfaces by using the k-phase of Al<sub>2</sub>O<sub>3</sub> which shows a multicoordination of both Al and O atoms and a lower density with respect to the other phases. These properties make the k-phase well representative of the experimentally observed amorphous Al<sub>2</sub>O<sub>3</sub>. Our (In)GaAs(001)/k-Al<sub>2</sub>O<sub>3</sub>(011) interface model is defect-free and strictly satisfies the electron counting rule. The model structure is then suitably modified to incorporate defects that might occur at the interface. Within this theoretical framework we find both the As-As dimer and the Ga dangling bond defect states to lie at ~ 0.3 eV below the GaAs conduction-band edge. We then address the energy levels of these defects at the InGaAs/Al<sub>2</sub>O<sub>3</sub> interface by considering local environment with differing In content. In all cases considered, the As-As dimer and the Ga dangling bond levels are found to lie well above the conduction band of InGaAs.

### ***Microscopic description of the phases of BaTiO<sub>3</sub> and related perovskites***

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Even if ferroelectric materials like BaTiO<sub>3</sub> and KNbO<sub>3</sub> have been used for over fifty years, their microscopic behavior is still debated, like for instance the description of the nature of the ferroelectric-paraelectric phase transition (displacive vs. order-disorder). Moreover, even in the cubic phase, the prototypical 5-atom unit cell that is usually used to describe ABO<sub>3</sub> perovskites does not provide the correct microscopic picture for materials like BaTiO<sub>3</sub>, where instead Ti atoms are displaced with respect to the center of the octahedral cage of oxygens, creating local dipoles (that average to zero on a larger cell) contrary to what is typically assumed in most simulations. However, this is not the case for other ABO<sub>3</sub> systems. Therefore, we present here some results from total-energy and molecular dynamics calculations over the family of ABO<sub>3</sub> perovskites, that aim at clarifying the behavior of these materials and assess the driving mechanisms that govern the different phases.

### ***Fermi-level pinning in GaAs: a hybrid functional study***

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To understand the origin of Fermi-level pinning at GaAs/oxide interfaces, we address intrinsic and oxygen-related amphoteric defects in GaAs using a hybrid density-functional scheme [1-3]. Amphoteric defects lead to Fermi-level pinning because of their dual behavior as donors and acceptors. We propose a new defect complex in which an As antisite binds to a Ga vacancy. Its amphoteric behavior is associated to the bistability of the Ga vacancy which transforms to an As antisite plus As vacancy. The complex is found to be stable against dissociation and to cause Fermi-level pinning at 0.59 eV above the valence band maximum (VBM), in agreement with the experimental pinning level at 0.6 eV in highly damaged GaAs samples [1]. Upon O capture the defect complex loses its bistability as the O atom occupies the As vacancy. Structural and electronic behaviors of the resulting O defect, perfectly match the experimental characterization of the defect responsible for Fermi-level pinning in GaAs:O [2]. The defect still shows amphoteric behavior with stable +1 and -1 charge states. The pinning level is now found at 1.17 eV above the VBM, in excellent agreement with the experimental level at 1.1 eV in GaAs:O [4]. Furthermore, the optical transition energies between its charge states closely reproduce the experimental values [4].

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### **Structure and magnetic coupling in YBaFeCuO<sub>5</sub>**

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We theoretically study the structure and exchange couplings in multiferroic YBaFeCuO<sub>5</sub> (YBFCO). Using density functional theory we calculate energies of configurations with various Fe<sup>{3+}</sup>/Cu<sup>{2+}</sup> orderings in the bilayered perovskite structure of YBFCO. We find that configurations with different distribution of Fe<sup>{3+}</sup> and Cu<sup>{2+}</sup> ions fall into two groups with distinctly different energies. The energies of those in the lowest energy group are close to that of the ground state (relative to the growth temperature) suggesting Fe<sup>{3+}</sup> and Cu<sup>{2+}</sup> to be disordered in YBFCO. Finally, we calculate exchange coupling constants for all the low energy configurations and show that the magnetic ordering resulting from these couplings is compatible with the experimentally-observed high-temperature magnetic ordering. However, they do not explain the existence of the experimentally observed low-temperature incommensurate magnetic structure.

### **First-principles exploration of high energy facets of bismuth chalcogenide nanocrystals**

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Binary bismuth chalcogenides Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, and derived materials are currently justified as the reference topological insulators (TIs) due to their simple surface- state band structures (single Dirac cone) and relatively large bulk band gaps. Nanoscale TI materials are of particular interest as a large surface-to-volume ratio enhances the contribution of surfaces states, meaning they are promising candidates for potential device applications. So far, the vast majority of research efforts have focused on the low-energy (0001) surfaces which correspond to weak planes in the layered crystal structures. Low dimensional nanostructures (nanowires and nanoparticles) will inevitably involve higher energy facets. We perform a systematic ab-initio investigation of, firstly, the surfaces of bismuth chalcogenide TI nanostructures. These are characterized by different crystallographic orientations as well as local structures and stoichiometries. Secondly, we study the effect of surface orientation on the electronic structure and associated properties of Bi<sub>2</sub>Se<sub>3</sub> (Bi<sub>2</sub>Te<sub>3</sub>) nanostructures. We find several stable surfaces and, depending on the chemical potential value, predict the conditions favouring nanoplate and nanowire morphologies. Surface orientation is found to show a significant effect on the band dispersion and spin polarization of the topological surface-state charge carriers.

### **Thermomechanical properties of iron: model potentials and first-principles calculations**

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Stiffness tensors provide a full characterization of the mechanical response of crystals in the linear regime of stress-strain. Their prediction from empirical potentials can provide stringent tests for the validation of the potential model parametrization used to describe the underlying electronic interactions. In this work, we investigate the thermoelastic properties of  $\hat{\pm}$ -iron obtained from selected embedded atom potentials commonly used in the scientific community ([1], [2], [3], [4]). We show how, beyond the expected trivial agreement with experimental data at

low temperature (these data are included in the fitting training set), the reliability of the potentials become questionable in the high temperature regime. In the perspective of developing more accurate model potentials fitted on ab-initio data, we also investigate the elastic properties from first-principles. Interestingly, despite their good thermal behavior, the calculated elastic constants display remarkable relative errors with respect to experiments. These discrepancies highlight the difficulties of standard density functional theory in describing the system considered.

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### **Self-consistent continuum solvation model for the optical properties of complex molecular systems in solution**

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We present a new method to compute the optical properties of complex molecular systems in solution, based on Time-Dependent Density-Functional Theory [1], as implemented in the “turboTDDFT” component [2] of the Quantum ESPRESSO distribution, and the recently proposed revised self-consistent continuum solvation (SCCS) model [2], as implemented in the “environ” component of Quantum ESPRESSO [3]. In the spirit of the Polarisable Continuum Model (PCM) [4], the solvent is modelled by a continuous polarisable medium. At variance with it, however, the shape and size of the cavity hosting the solute is determined self-consistently depending on the molecular electron ground-state distribution. The new method, which has been implemented in the turboTDDFT component of Quantum ESPRESSO [3], has been benchmarked with a test on the 4-Aminophthalimide molecule in water, resulting in a remarkable agreement with the results obtained from the implementation of the PCM [3] in the Gaussian code [5].

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### **Atomistic modeling of the morphology and electron transport at a carbon nanotube-polyethylene junction**

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The conduction mechanism in carbon nanotube (CNT) polymer nanocomposites is closely connected to the morphology of the nanocomposite. There has been a considerable amount of work invested in understanding the role of the distribution of the CNTs in the composite and how it influences the conductivity. However, less interest has been devoted to the electron transport across a single CNT-polymer junction. We have therefore performed an atomistic study of the

electron transmission through a CNT-polyethylene(PE)-CNT junction[1]. The morphology and dynamics of the junction is modelled by classical molecular dynamics (MD) simulations, and transport properties are calculated by a non-equilibrium Green's function approach based on the density functional tight binding(DFTB) method. Many snapshot from the MD trajectories are used to calculate the transmission to obtain good statistics for the junction resistance and tunneling barrier. The calculations reveal that the electron transmission depends noticeably on the CNT-CNT separation and on the consequent polymer wrapping. In the near contact regime at CNT-CNT distances shorter than 6 Å, the polyethylene molecules do not penetrate in the space between the CNTs. This has the effect that the electron transmission proceeds via direct tunneling between the two CNTs across a vacuum region without relevant contribution from the surrounding polymer. For distances larger than 6 Å, the PE molecules enter into the junction region, such that the frontier orbitals of these PE molecules can couple to the CNT metallic states. This resonance tail increases the electron transmission probability between the CNTs across the junction by several orders of magnitude, thus lowering the effective barrier. These results indicate that the gradual interpenetration of the polymer molecules into the junction region divide the electron transmission between two adjacent CNTs in a composite into two distinct regimes.

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### ***The macroscopic monopolization in magnetoelectrics***

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We develop the formalism of the macroscopic monopolization - that is the monopole moment per unit volume - in periodic solids, and discuss its relationship to the diagonal magnetoelectric effect. For the series of lithium transition metal phosphate compounds we use first-principles density functional theory to calculate the contributions to the macroscopic monopolization from the global distribution of magnetic moments within the unit cell, as well as from the distribution of magnetization around the atomic sites. We find one example within the series (LiMnPO<sub>4</sub>) that shows a macroscopic monopolization corresponding to a ferromonopolar ordering consistent with its diagonal magnetoelectric response. The other members of the series (LiMPO<sub>4</sub>, with M = Co, Fe and Ni) have zero net monopolization but have antiferromonopolar orderings that should lead to q-dependent diagonal magnetoelectric effects.

### ***Simulating electron energy loss spectroscopy in large systems***

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Electron Energy-Loss Spectroscopy (EELS) and Inelastic X-ray scattering (IXS) are the methods of choice to sample collective charge excitations (plasmons) in solids. The strong dependence of plasmon dynamics on the size and shape of nano-structured devices holds the promise of an extraordinary control over their optical properties. When the distances between the nanoscale components in the device are themselves nano-metric, quantum effects must be taken into account, and a fully quantum-mechanical description is called for. The EELS and IXS cross sections are proportional to the imaginary part of the diagonal elements of the inverse dielectric matrix, which can be computed using Time-Dependent Density Functional Theory (TDDFT) [1]. Current TDDFT-based approaches to dynamical screening involve the computation of single-particle unoccupied states and the manipulation (multiplication, inversion) of large matrices [2], two tasks that make these approaches unfit to address systems larger than a handful of atoms. We present a new method, based on the iterative solution of the TDDFT

equations within first-order perturbation theory, that avoids these difficulties by using a Lanczos recursion technique and adopting a representation of the response orbitals borrowed from density-functional perturbation theory [3]. The resulting algorithm allows to compute the EELS and IXS cross sections for a same transferred momentum and over an entire, wide, frequency range with a numerical workload comparable to a single ground-state DFT calculation. Our method has been implemented in the `extsc{Quantum ESPRESSO}` distribution of computer codes [4], and successfully tested on prototypical examples, such as silicon and aluminum. As a new application, we present results for the semimetal bismuth, where spin-orbit effects play a prominent role.

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## **Energetic stability and chemical reactivity of the graphene/SiC(0001) interface from first principles**

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High-quality graphene grown epitaxially on SiC(0001) can be regarded as a convenient template for the realization of graphene-based electronics [1]. However, the presence of a carbon "buffer" layer buried at the interface between the SiC surface and the epitaxial graphene is detrimental to the electronic transport properties of the latter. Hydrogen intercalation at high temperatures can be used to convert the buffer layer into a quasi-free standing graphene layer lying directly above a H-saturated SiC(0001) surface, which provides a much more effective decoupling from the substrate [2]. In this work, we address the energetic stability and the chemical reactivity of the graphene/SiC(0001) interface through density functional theory simulations of commensurate models presenting very low graphene strain [3]. The interface stability is found to be proportional to the extent of the atomic-scale corrugation, which indicates a partial  $sp^2$  to  $sp^3$  rehybridization (pyramidalization) of the Si-bonded C atoms in the buffer layer [4]. While the number of C-Si covalent bonds at the interface stays approximately constant from one model to the other, their relative stability can be interpreted, also quantitatively, through the pyramidalization angles of those C atoms [4]. We also find that the remaining C atoms show a chemical reactivity significantly higher than in free-standing graphene. H-binding energies onto the threefold-coordinated C atoms of the buffer are three-to-four times larger than on graphene [5], while  $H_2$ -splitting becomes an exothermic process, with activation barriers that can be up to four times smaller than on graphene.

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## **Implementation of image charges in QM/MM**

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A method for including polarization effects within hybrid quantum mechanics/molecular mechanics (QM/MM) simulations of 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 an empirical 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] and for a comprehensive description of processes at electrode interfaces [2]. In this work, the image charge method was implemented in the QM/MM module of the CP2K program package. The implementation is based on the Siepmann-Sprick scheme [3], 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 structural and electronic effects due to the introduced polarization were studied for benzene, nitrobenzene and DNA bases adsorbed at Au(111) as well as for water on Pt(111). Large-scale molecular dynamics simulations of a water film in contact with a Pt(111) surface show that our method is suitable for simulations of liquid/metal interfaces at reduced computational cost [4].

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### ***A workshop memoir: implementing the converse approach to NMR chemical shifts using Quantum ESPRESSO***

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While orbital magnetization for atoms and molecules is a well defined and easy to calculate property, it is not straightforward to compute it in solids, due to the ill-defined nature of the position operator in extended systems. This challenge was overcome recently with the development of the modern theory of orbital magnetization [1], allowing one to calculate the orbital magnetization directly from the ground-state wavefunctions of a solid. Following this development, an alternative way to calculate NMR chemical shifts using the orbital magnetization has been formulated [2]. This approach (called "converse", at variance to the well-established "direct" linear-response approach [3]) has been shown to successfully reproduce experimental and previous theoretical results. Notably, it is highly efficient in the case of large systems with few atomic sites of interest [4] and it has the potential to be extended straightforwardly to advanced exchange-correlation functionals (e.g. hybrids or DFT+U), for which a linear-response approach would be too cumbersome. During the "Advanced Quantum Espresso Developer Training" workshop held in ICTP in December 2013, the participants joined a common development project to implement the converse approach to NMR in Quantum ESPRESSO. We validated implementation on several test cases, using norm-conserving pseudopotentials, and started preliminary work to extend the approach to the case of ultrasoft pseudopotentials and PAW datasets.

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## **Existence and properties of minimizers for Kohn-Sham within the local-spin-density-approximation**

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The Density Functional Theory transforms the high-dimensional Schrödinger problem into a problem based on electronic density (or spin density matrix [1] in the spin setting). In the Kohn-Sham approximation, this transformation introduces an unknown term, namely the exchange-correlation energy that we have to approximate. One of the most used approximation is the Local (Spin) Density Approximation. Throughout those approximations, some physical properties could be lost. In particular, the existence of a solution is no longer certain. Following [2], we will discuss the existence and properties of such solutions as we include the spin variable.

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## **What Koopmans-compliant functionals can do for you: a comprehensive benchmark of the G2-set and organic photovoltaics**

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The purpose of this work is to explain the theoretical background of Koopmans-compliant (KC) functionals [1,2,3], and to present an overview of their performance when applied to the calculation of thermochemical and electronic excitation properties of materials. After a theoretical introduction, we present a comprehensive benchmark for all flavors of KC functionals on the whole G2-set. Results for ionization energies, molecular geometries, and atomization energies are compared not only to conventional density-functional (such as: LDA, PBE) results, but also to orbital-density dependent calculations with the Perdew-Zunger self-interaction correction, and -- where available -- to GW results. We also assess the performance of KC functionals in computing ionization energies and electron affinities of a set of molecules which are relevant for the construction of organic photo-active devices (among which fullerenes, acenes and phthalocyanines). Some of their photoemission spectra are also shown, and compared with experiment. In the case of Zn-phthalocyanine, a comparison with recent non-self-consistent GW results is also available.

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## ***Cosmic strings meet multiferroics: understanding topological defect formation in crystals.***

**Sinead Griffin**[1], Martin Lilienblum, Manfred Fiebig, Nicola Spaldin  
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Jumping from the expanse of galactic scales to land in the laboratory might seem a gargantuan task. Common to both, however, is the the concept of symmetry breaking and in particular the formation of topological defects. Here I discuss the formation of topological defects in multiferroic YMnO<sub>3</sub> whose ferroelectric behavior enables the direct imaging of these defects. I also show how this material can be used to study the Kibble-Zurek model of topological defect formation in the early universe and give quantitative insights on the number of domains formed during the spontaneous symmetry breaking phase transition. We also uncover a surprising 'beyond Kibble-Zurek' behaviour, and discuss this in the context of the material's properties.

## ***High-throughput screening with the aida framework: the case of solid-state lithium conductors***

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In recent years much attention has been given to high-throughput techniques for materials' discovery and characterization, a complex challenge where state-of-the-art theoretical advancements meet data analytics and automated job management. We present here one of the first high-throughput projects done with our AiiDA framework (Automated Interactive Infrastructure and Database for Atomistic simulations) [1], an open-source infrastructure built for largely automatic materials' design and discovery. Starting from the ICSD database, we build an automatic workflow to compute lithium-ion diffusion with Car-Parrinello molecular dynamics. This specific workflow, comprising of an initial ground-state variable-cell relaxation followed by a microcanonical simulation, is an example of the high level of automation one can reach through AiiDA and the most important technical features on how to implement flexible and robust research workflows will be discussed.

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## ***Finite size effects in dft calculations of neutral point defect properties: a corrective scheme***

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Point defects and their clusters are known to strongly affect material characteristics, like kinetics and mechanical behaviours. Modelling their properties at an atomic scale requires to take special care of the long range atomic relaxations. Indeed, this elastic field can strongly affect the calculated properties in atomistic simulations, because of the finite size of the system under study. This is an important restriction for ab initio methods which are limited to a few hundred atoms. This kind of issue is well known charged defects [1,2], where electrostatic interactions exist, but the case of neutral defects was not considered until now. We propose an original approach that couples ab initio calculations and linear elasticity theory to get rid of this limitation [3]. The reliability and benefit of our approach are demonstrated for materials with different structures and behaviours: the self-interstitial in hcp zirconium, clusters of height interstitials in bcc iron and the vacancy in diamond silicon. Our corrective scheme greatly improves the convergence of the calculated properties, allowing one either to study larger defects by DFT, or to use DFT methods that are more cumbersome but more accurate for the system under study.

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## ***Approximated self-energy formulations for electron-magnon coupling effects***

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Ground state properties and low-lying excitations in magnetic materials are an emergent feature of the electronic degree of freedom. In some energy regimes it is possible to describe the latter as slowly precessing deviations from a reference direction, or spin waves[1]; closer to a critical temperature instead, a disordered local moment picture can be more appropriate[2]. It may be possible to also consider the problem from the opposite perspective, of how initially well-defined electronic states respond to the ability to excite or extinguish such deviations from a reference scenario. When considering excitations hosted on the ionic subsystem, or phonons, theoretical tools have been developed to describe at various level of sophistication how Bloch states respond to such way of effectively exchanging energy and momentum[3]. We try here to examine ways to treat the formally analogous problem posed by transverse magnons, which are supposed to also give rise to electronic structure renormalization effects expressible by a self-energy correction term[4,5,6]. Similarities and differences between the two scenarios are briefly outlined, and approximated strategies for looking at the problem put forward for review.

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## ***Dynamical crossover at the liquid-liquid transformation of a compressed molten alkali metal***

**Ari P Seitsonen**[1], Taras Bryk [2,3], Simone De Panfilis [4,2], Federico A Gorelli [5,6], Eugene Gregoryanz [7], Michael Krisch [8], Giancarlo Ruocco [2,6], Mario Santoro [9], Tullio Scopigno [2,6]

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Density-driven phase transformations are a known phenomenon in liquids. Pressure-driven transitions from an open low-density to a higher-density close-packed structure were observed for a number of systems. Here, we show [1] a less intuitive, inverse behaviour. We investigated the electronic, atomic, and dynamic structures of liquid Rb along an isothermal line at 573 K, at 1.2–27.4 GPa, by means of ab initio molecular dynamics simulations and inelastic X-ray scattering experiments. The excellent agreement of the simulations with experimental data performed up to 6.6 GPa validates the overall approach. Above 12.5 GPa, the breakdown of the nearly-free-electron model drives a transition of the pure liquid metal towards a less metallic, denser liquid, whose first coordination shell is less compact. Our study unveils the interplay between electronic, structural, and dynamic degrees of freedom along this liquid-liquid phase transition. In view of its electronic nature, we believe that this behaviour is general in the first



group elements, thus shedding new light into the high-pressure properties of alkali metals.

[1] "Dynamical crossover at the liquid-liquid transformation of a compressed molten alkali metal", Taras Bryk, Simone De Panfilis, Federico A Gorelli, Eugene Gregoryanz, Michael Krisch, Giancarlo Ruocco, Mario Santoro, Tullio Scopigno and Ari Paavo Seitsonen, *Physical Review Letters* 111, 077801 (2013); DOI: 10.1103/PhysRevLett.111.077801

### **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 (GBs), the intrinsic topological defects in polycrystalline materials, are expected to strongly affect the electronic transport properties of graphene [4]. The poster presents our systematic investigation of the ballistic transmission of charge carriers through the one-dimensional grain-boundary defects within the tight-binding model framework and the Landauer-Büttiker formalism. First, the relations between the structure of regular GBs and their electronic transport properties reveal a number of surprising results such as the suppression of the transmission of low-energy charge carriers. This counter-intuitive behavior is explained from the standpoint of resonant backscattering involving localized electronic states of topological origin [5]. Second, a Monte-Carlo approach is presented for the systematic exploration of the configuration space of disordered GBs. Structure-property relations found in the simulations of disordered grain boundaries will be discussed [6].

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