Total Energy and Force Methods

Workshop 2016

University of Luxembourg

11 – 13 January 2016

UNIVERSITÉ DU LUXEMBOURG

Fonds National de la Recherche Luxembourg

EUROPEAN SCIENCE FOUNDATION

Total Energy and Force Methods, January 11-13, 2016, Luxembourg

The workshop focuses on the most recent developments in the field of electronic-structure methods from the first-principles perspective and their diverse applications. It is organized within the "mini" series associated to the "Total Energies and Forces" conference, held at ICTP in Trieste every two years. While the Trieste conferences take place on odd-numbered years since 1987, the alternates are held on even-numbered years, each time in a different location. The previous most recent workshops of this series took place in Madrid (2000), Tenerife (2002), Paris (2004), Cambridge (2006), Bonn (2008), Shanghai (2010), Barcelona (2012), and Lausanne (2014).

The numerous approaches that are developed and used in the electronic-structure community provide the foundation for computing many physical and chemical properties of solids, liquids, and low-dimensional systems. However, there are numerous challenging applications for which the level of approximation is insufficient or where computational costs are prohibitive for accurate quantitative prediction of material properties. Therefore, continued efforts are devoted to an improvement of existing methods and the development of new methods.

The core areas for the conference are:
(i) Theory and methods: *Density-functional theory, time-dependent DFT, many-body techniques for real materials, quantum Monte Carlo, ab-initio molecular dynamics, large scale and multiscale simulations, quantum-chemistry methods.*
(ii) Applications: *nanoscience, biochemistry and biomaterials, magnetism and spintronics, geophysics, functional materials, surfaces, spectroscopies, catalysis and electrochemistry, chemical reactions and kinetics, materials design.*

The program committee (international advisory board) has tried to arrange a scientific program covering some of the most recent highlights in the field and giving the word in particular to (relatively) young researchers. We encourage active participation of everybody in the discussions after each talk. The central part of the workshop is the poster session on Monday afternoon. Posters can remain on the poster boards during the whole duration of the workshop, giving additional time for presentation and discussion of research results.

Finally, we hope that you will find some time to enjoy the city of Luxembourg. For this purpose, we offer a guided evening walk through the old city on Tuesday, right before the conference dinner.

Organizers and Advisory Board

Local organizers

- Ludger Wirtz (University of Luxembourg)
- Xavier Blase (Institut Néel, Grenoble),
- Francesco Mauri (Université Pierre et Marie Curie, Paris),
- Matteo Calandra (Université Pierre et Marie Curie, Paris).

International advisory board

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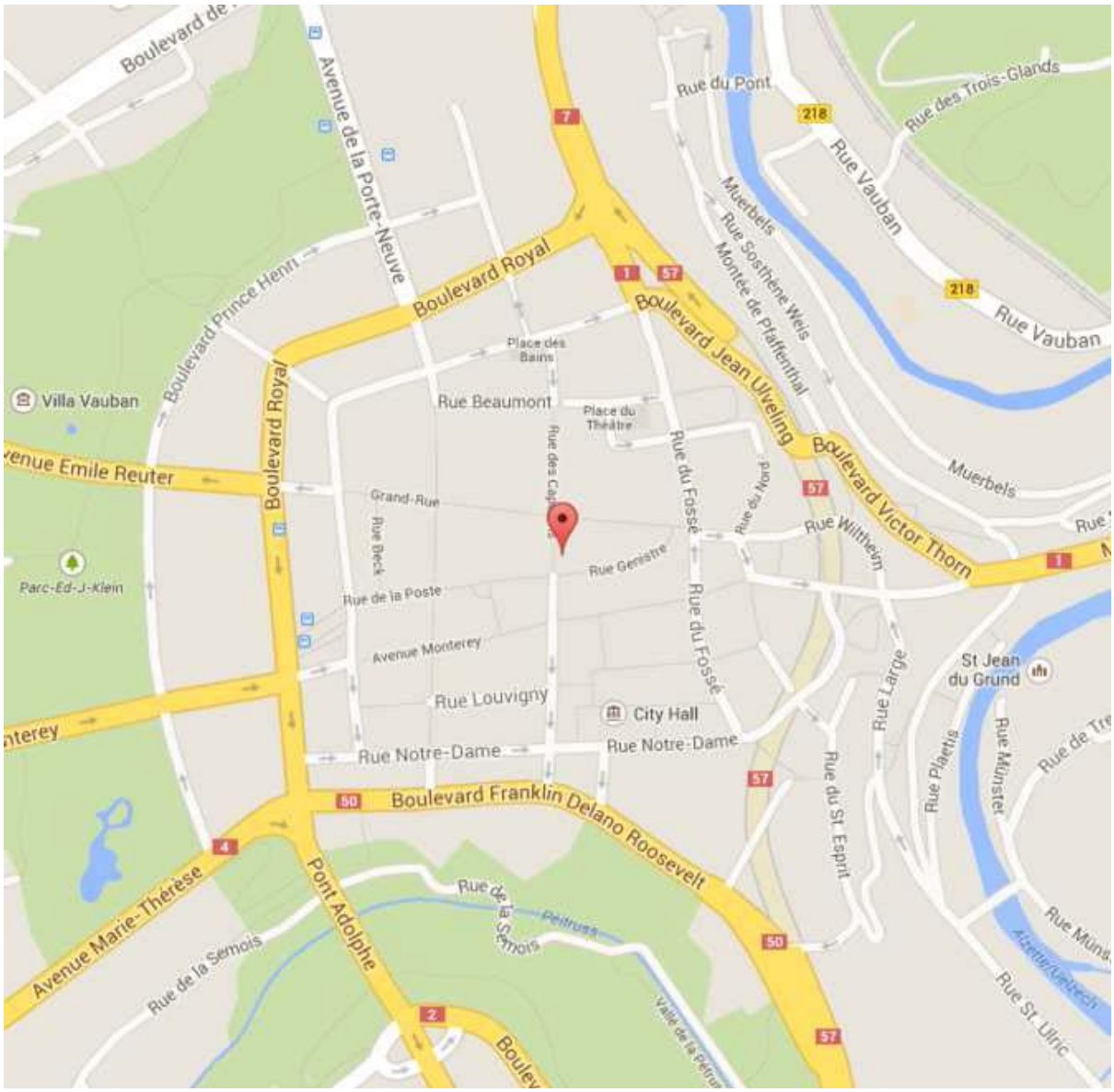
Funding

Some useful information

Map of the center of Luxembourg:



Internet:

At the conference site there is a specific wireless network for the time of the conference, please connect to SSID: totalenergy with the password totalenergy@UL2016.

Social dinner and city tour on Tuesday:

A guided night-city-tour will leave from “Place d’Armes” at 5.45 pm. The guide will bring the groups directly in front of the “Brasserie du Cercle”, Rue des Capucins 2 (see map above) where the Social Dinner will be served starting at 7.30 pm. In case you forgot your menu choices, you can find them on the back of your badge.

Conference venue:

The conference will be held in room BS 003 located in the “Bâtiment des Sciences”.

Lunch:

Lunch will be served every day at Restaurant Porta Nova located at 14 Avenue de la Faïencerie, 15 minutes walking distance from the Campus.

For any information you might need, please send us an e-mail on info.totalenergy@uni.lu or contact Frederique Bertrand onsite.

09:00-09:30 Opening remarks
Ludger Wirtz, Local organizer;
Paul Heuschling, Dean of faculty of Science and Technology, University of Luxembourg;
Christiane Kaell, Fonds National de la Recherche

Ferroic materials

09:30-10:00 Jorge Íñiguez *(Luxembourg Institute of Science and Technology, Belvaux, Luxembourg)*
Realistic large-scale simulations of materials with non-trivial lattice-dynamical and electronic properties)

10:00-10:30 coffee break

DFT-functionals

10:30-11:00 Alexandre Tkatchenko *(FHI Berlin, Germany, University of Luxembourg, Luxembourg)*
Electronic Properties of Molecules and Materials with a Self-Consistent Interatomic van der Waals Density Functional)

11:00-11:30 Ngoc Linh Nguyen *(EPFL, Lausanne, Switzerland)*
First-Principles Photoemission Spectroscopy in Molecules and Electronic Structure of Extended Systems from Koopmans-Compliant Functionals

11:30-12:00 Ryotaro Arita *(RIKEN, Japan)*
Density functional theory for plasmon-assisted superconductivity

12:00-14:00 Lunch Break

Coupled-cluster and QMC : learning from chemistry

14:00-14:30 Klaus Doll *(University of Ulm, Germany)*
Extrapolating accurate wave-function based energies from clusters to bulk

14:30-15:00 George Booth *(King's College London, United Kingdom)*
Stochastic quantum chemistry for molecules and solids)

15:00-15:30 Andreas Grüneis *(Max-Planck-Institute for Solid State Research, Stuttgart, Germany)*
Towards Efficient Coupled Cluster Theories for Solids

15:30-16:00 coffee break

Layered Systems

16:00-16:30 Sébastien Lebègue *(Université de Lorraine/CNRS, France)*
New two dimensional compounds: beyond graphene

16:30-17:00 Maria Hellgren *(IMPMC, Paris, France)*
Impact of electronic correlation on the charge density wave instability in TiSe2)

17:00-20:00 Poster session (with light snacks)

Electron-phonon interaction

09:00-09:30 Matthieu Verstraete *(University of Liège, Belgium)*
Ab initio phonon limited transport

09:30-10:00 Lilia Boeri *(Graz University of Technology, Austria)*
High-pressure hydrides: conventional high-Tc superconductors

10:00-10:30 coffee break

Excited-state dynamics

10:30-11:00 Marco Bernardi *(California Institute of Technology, Pasadena, USA)*
Ultrafast Dynamics of Excited Electrons in Materials

11:00-11:30 Carlo Andrea Rozzi *(CNR, Modena, Italy)*
Ultrafast charge separation dynamics in photovoltaic heterojunctions

11:30-12:00 Federica Agostini *(MPI Halle, Germany)*
Coupled Electron-Nuclear Dynamics in Non-Adiabatic Processes

12:00-14:00 Lunch Break

Green's function methods/ MBPT

14:00-14:30 Michiel van Setten *(UC Louvain, Belgium)*
GW and molecules: a benchmark for G0W0 and developments beyond

14:30-15:00 Manish Jain *(IISC, Bangalore, India)*
Improved quasiparticle wave functions and mean field for G0W0 calculations

15:00-15:30 Eran Rabani *(Department of Chemistry, University of California, Berkeley)*
Stochastic Approaches to Electronic Structure: From DFT and TDDFT to GW and BSE

15:30-16:00 coffee break

Random Phase Approximation

16:00-16:30 Thomas Olsen *(DTU, Denmark)*
Total energy calculations beyond the Random Phase Approximation

16:30-17:00 Dario Rocca *(Université de Lorraine, Vandoeuvre-lès-Nancy, France)*
Dielectric matrix formulation of correlation energies in the Random Phase Approximation: Inclusion of exchange effects

17:45-19:15 Guided walk through the old city of Luxembourg

19:30 Conference dinner

Exploring energy surfaces and phase space (MD)

09:00-09:30 Fabio Pietrucci *(Université Pierre et Marie Curie – Sorbonne, Paris, France)*
A unified approach to reactions in gas phase and solution via topological coordinates

09:30-10:00 Robert Baldock *(University of Cambridge, United Kingdom)*
Calculating the pressure-temperature phase diagrams of materials

Applications of DFT

10:00-10:30 Victor Pardo *(Universidade Santiago de Compostela, Spain)*
Layered iridates: a discussion on noncollinear vs collinear treatment of 5d electron systems

10:30-11:00 Jean-Sébastien Filhol *(Université de Montpellier, Montpellier, France)*
Using the electrochemical dimension for modelling surface and interfaces for energy materials

Invited Talks

Jorge Íñiguez
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Realistic large-scale simulations of materials with non-trivial lattice-dynamical and electronic properties

Jorge Íñiguez

I will describe recent methodological advances initially motivated by our interest in functional materials, in particular ferroelectric and ferroelastic perovskite oxides. A realistic investigation of such compounds mandatorily requires: (1) large-scale simulations (e.g., to address the multi-domain configurations ubiquitous in ferroics), (2) incorporating thermal effects (e.g., to investigate temperature-driven transitions and activated phenomena), and (3) with DFT-like accuracy (as the effects of interest are often controlled by energy differences of a few meV per atom). In this talk I will present our work to develop first-principles-based lattice-dynamical models that satisfy all these requirements. I will discuss applications (to unveil structural transitions occurring within ferroelectric domains walls, to explain the origin of a striking negative-capacitance effect in ferroelectric/dielectric superlattices) that illustrate the predictive power of the new models and their ability to go beyond the state of the art of the field. Time allowing, I will also describe a strategy to incorporate (the relevant) electronic degrees of freedom in the model simulations. I will illustrate the resulting approach with applications to physically non-trivial cases (interface-confined electron gases, magnetic order in strongly-correlated oxides), showing that it allows us to obtain DFT-like accuracy at a much reduced computational cost. Work done in collaboration with many colleagues, especially: Pablo Garcia-Fernandez and Javier Junquera (U. Cantabria, Spain) on the development of the scheme that incorporates electrons; Carlos Escorihuela-Sayalero (Luxembourg Institute of Science and Technology) and Jacek C. Wojdel (Institute de Ciencia de Materials de Barcelona, Spain) on the lattice-dynamical models.

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Electronic Properties of Molecules and Materials with a Self-Consistent Interatomic van der Waals Density Functional

Alexandre Tkatchenko

Long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems, ranging from small dimers to complex hybrid inorganic/organic interfaces (HIOS). However, how strong is the effect of vdW interactions on the electronic properties of molecules and extended systems? It is often argued that the vdW energy has a small, or even negligible, influence on the electron density, n(**r**), and derived electronic properties, since the vdW energy represents only a tiny fraction (0.001%) of the total electronic energy.

To answer the question posed above, we derived a fully self-consistent (SC) implementation of the density-dependent interatomic vdW functional of Tkatchenko and Scheffler [1] and its extension to surfaces [2]. Not surprisingly, vdW self-consistency leads to tiny modifications of the structure, stability, and electronic properties of molecular dimers and crystals. However, unexpectedly large effects are found in the binding energies, distances and electrostatic moments of highly polarizable alkali metal dimers. Most importantly, vdW interactions produced complex and sizable electronic charge redistribution in the vicinity of metallic surfaces and at organic/metal interfaces. As a result, for several coinage metal (111) surfaces, self-consistency induces modifications in the surface dipole, leading to an increase of up to 0.30 eV in the computed work functions. Furthermore, in the case of HIOS, SC vdW entails modifications of up to 0.22 eV in the shift of the interface workfunction, a property induced by molecular adsorption. The underlying mechanism responsible for the workfunction modifications stems from an interplay between two effects driven by SC vdW interactions: (i) the modification of the interface dipole, and (ii) a reduction in the charge transfer between the molecule and the surface.

The analysis of self-consistent vdW effects performed in this work demonstrates the importance of vdW interactions on the electronic properties of different classes of systems, with self-consistency systematically improving the agreement between the theoretical predictions and the experimental measurements. Our study reveals a nontrivial connection between electrostatics and long-range electron correlation effects [3].

A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, Phys. Rev. Lett. 108, 146103 (2012).
N. Ferri, R. A. DiStasio Jr., A. Ambrosetti, R. Car, and A. Tkatchenko, Phys. Rev. Lett. 114, 176802 (2015).

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First-Principles Photoemission Spectroscopy in Molecules and Electronic Structure of Extended Systems from Koopmans-Compliant Functionals

Ngoc Linh Nguyen, Giovanni Borghi, Nicola Colonna, Ismaila Dabo, Andrea Ferretti, and Nicola Marzari

While density functional theory (DFT) provides an efficient and reliable method for computing the ground state energetics for a wide variety of materials, the eigenstates obtained by solving the Kohn-Sham equation do not formally correspond to charged excitation energies. This is particularly evident when comparing photoemission spectra, computed with the local or semi local exchange correlation functionals, with experiments. In this work, we show that Koopmans-compliant functionals [1,2], constructed to enforce piecewise linearity in energy functionals with respect to fractional occupations - i.e., with respect to charged excitations - can predict not only frontier ionization potentials and electron affinities of molecules with an accuracy comparable with that of higher-level quantum chemistry and many-body perturbation methods but also molecular photoemission spectra and momentum maps of Dyson orbitals, that are shown to be in excellent agreement with experimental ultraviolet photoemission spectroscopy and orbital tomography data [3]. These results highlight the role of Koopmans-compliant functionals as accurate and inexpensive quasiparticle approximations to the spectral potential [4]. Furthermore, we discuss how to apply these functionals to extended systems, with results for semiconductor band gaps and band structures.

[1] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, M. Cococcioni, PRB 82, 115121 (2010)
[2] G. Borghi, A. Ferretti, N.L. Nguyen, I. Dabo, N. Marzari, PRB 90, 075135 (2014).
[3] N.L.Nguyen, G. Borghi, A. Ferretti, I. Dabo, N. Marzari, PRL 114, 166405 (2015).
[4] A. Ferretti, I. Dabo, M. Cococcioni, N. Marzari, PRB 89, 195134 (2014).

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Density functional theory for plasmon-assisted superconductivity

Ryosuke Akashi, Ryotaro Arita

Density functional theory for superconductors (SCDFT) is one of the most promising approaches to evaluate the transition temperature (T_c) of superconductors from first principles. The scheme formulated by Gross et al. [M. Lüders et al., Phys. Rev. B 72, 024545 (2005), M. A. L. Marques et al., Phys. Rev. B 72, 024546 (2005)] has been successfully applied to various conventional phonon-mediated superconductors. In this conventional SCDFT, the screened Coulomb interaction is treated within the static approximation. On the other hand, it has been theoretically proposed that the dynamical structure of the screened Coulomb interaction can enhance the pairing instability. For example, in doped band insulators, plasmons are expected to play a crucial role in the superconductivity. Recently, we formulated a new scheme for plasmon-assisted superconductivity, and applied it to "high T_c" lithium under high pressures (T_c~20K). We found that plasmons significantly enhance Tc, and the agreement between theory and experiment becomes better.

R. Akashi and R. Arita, Phys. Rev. Lett., 111 057006 (2013)
R. Akashi and R. Arita, J. Phys. Soc. Jpn. 83 061016 (2014)

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Extrapolating accurate wave-function based energies from clusters to bulk

K. Doll

The total energy of a solid is the sum of the Hartree-Fock energy and the correlation energy. The calculation of the Hartree-Fock energy has become routine from around 1980 on. The calculation of the correlation energy on the other hand is still a challenging task, and usually density functional theory is employed. In [1], it was shown that ab-initio quantum-chemical methods (e.g. the coupled-cluster approach) are not necessarily restricted to molecules, but can be applied to calculate cohesive energies of solids. In the case of semiconductors, this is achieved by expanding the correlation energy as a sum of increments defined in terms of localized bonds. The method had been extended to the case of ionic solids [2], where the increments are based on correlation energies of the individual ions. The correlation contributions are computed with the code MOLPRO, employing clusters to model the bulk. The Hartree-Fock energy is independently computed with the code CRYSTAL.

[1] H. Stoll, Phys. Rev. B 46, 6700 (1992)
[2] K. Doll, M. Dolg, P. Fulde, H. Stoll, Phys. Rev. B 52, 4842 (1995)

George Booth
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Stochastic quantum chemistry for molecules and solids

G. Booth

In this talk, we will consider new techniques for the stochastic optimization of an explicit wave-function expansion for correlated systems. This will allow for essentially exact results in previously inaccessible quantum systems, for both the total energy, as well as important properties of the system. We will also chart how we can use this approach to go from molecular systems into the solid state, by combining the method with embedding procedures defined in an energy space or real space, to yield a powerful hybrid approach for correlated materials.

Thomas et al, J. Chem. Theory Comput., 2015, 11 (11), pp 5316–5325
Booth et al, Nature 493, 365–370 (2013)
Booth et al, Phys. Rev. B 91, 155107 (2015)
Booth et al, J. Chem. Phys., 131 , 054106, (2009)

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Towards Efficient Coupled Cluster Theories for Solids

A. Grüneis, F. Hummel, T. Gruber, T. Tsatsoulis

Quantum chemical wavefunction based methods like coupled cluster theories allow for very accurate solutions to the many-electron Schrödinger equation. The main advantage of wavefunction based methods is their ability to obtain systematic approximations to the exact many-electron correlation energy, albeit at a relatively large computational cost. This presentation will overview recent progress in applying coupled cluster methods to solids and techniques to reduce their computational cost such as explicit correlation methods and efficient one-electron basis sets. The discussed applications include the study of structural solid-solid phase transitions, defect formation energies and molecular adsorption on surfaces.

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New two dimensional compounds: beyond graphene

S. Lebègue

In the field of nanosciences, the quest for materials with reduced dimensionality is only at its beginning. While a lot of effort has been put initially on graphene, the focus has been extended in the last past years to functionalized graphene, boron nitride, silicene, and transition metal dichalcogenides in the form of single layers. Although these two-dimensional compounds offer a larger range of properties than graphene, there is a constant need for new materials presenting equivalent or superior performances to the ones already known.

During this talk, I will present an approach that we have used to discover potential new two-dimensional materials. This approach corresponds to perform data mining in the Inorganic Crystal Structure Database using simple geometrical criteria, and allowed us to identify nearly 40 new materials that could be exfoliated into two-dimensional sheets. Among this list, we found that Cu_2S could indeed be obtained in the form of quasi-isolated layers, with a bandgap of 0.9 eV using the GW approximation. I will also present some of our recent results concerning the electronic structure of various indium selenides two dimensional compounds.

S. Lebègue, T. Bjorkman, M. Klintenberg, R. M. Nieminen, and O. Eriksson, Phys. Rev. X. 3, 031002 (2013)
F. Ben Romdhane, O. Cretu, L. Debbichi, O. Eriksson, S. Lebègue, and F. Banhart, Small 11, 1253 (2015)
L. Debbichi, O. Eriksson, and S. Lebègue, J. Phys. Chem. Letters 6, 3098 (2015)

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Impact of electronic correlation on the charge density wave instability in $TiSe_2$

Maria Hellgren, Raffaello Bianco, Matteo Calandra, Francesco Mauri, Ludger Wirtz

Titanium diselenide ($TiSe_2$) is a layered material exhibiting several interesting properties. At low temperature it undergoes a charge density wave (CDW) instability and upon Cu-intercalation or the application of pressure the CDW is suppressed and superconductivity emerges. The role of electronic correlation in these phase-transitions is expected to be important but still not well understood. Local functionals within density functional theory can predict an instability but the band structure is in disagreement with angle-resolved photo emission spectra (ARPES). We have performed GW calculations and calculations with nonlocal hybrid functionals and find a qualitative improvement in terms of the orbital occupations. The importance of self-consistency within GW is highlighted and we discuss the role of the parameters within the hybrid functional. Finally, we show how the improved description of the electronic structure influence the vibrational properties and the CDW instability.

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Ab initio phonon limited transport

Matthieu Verstraete

We revisit the thermoelectric (TE) transport properties of two champion materials, PbTe and SnSe, using fully first principles methods. In both cases the performance of the material is due to subtle combinations of structural effects, scattering, and phase space reduction.

In PbTe anharmonic effects are completely opposite to the predicted quasiharmonic evolution of phonon frequencies and to frequently (and incorrectly) cited extrapolations of experiments. This stabilizes the material at high T, but also tends to enhance its thermal conductivity, in a non linear manner, above 600 Kelvin. This explains why PbTe is in practice limited to room temperature applications.

SnSe has recently been shown to be the most efficient TE material in bulk form. This is mainly due to a strongly enhanced carrier concentration and electrical conductivity, after going through a phase transition from 600 to 800 K. We calculate the transport coefficients as well as the defect concentrations ab initio, showing excellent agreement with experiment, and elucidating the origin of the double phase transition as well as the new charge carriers.

[1] Thermal conductivity in PbTe from first principles, AH Romero, EKU Gross, MJ Verstraete, and O Hellman, Physical Review B 91, 214310 (2015).

[2] Thermal stabilization and transport properties of SnSe from First Principles, A Dewandre, O Hellman, S Bhattacharya, AH Romero, GKH Madsen, and MJ Verstraete, unpublished.

[3] Lattice dynamics of anharmonic solids from first principles, O. Hellman, I. A. Abrikosov, and S. I. Simak, Physical Review B 84 180301 (2011).

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High-pressure hydrides: conventional high-T_c superconductors

Lilia Boeri

Last year's report of superconductivity with a record critical temperature (T_c) of 203 K in ultra-dense hydrogen sulphide (SH_3) [1] has confirmed Ashcroft's long-standing prediction of high-T_c conventional superconductivity in hydrogen-rich solids at high pressures. [2] This has stimulated an intense theoretical activity aimed at understanding the material-specific aspects underlying the high T_c of SH_3 [4], and identifying other potential high-T_c superconducting hydrides.[3]
In this talk I will discuss how chemical bonding and electronic structure influence the superconducting properties of sulfur and phosphorus hydrides, which are to date the only two conventional superconductors with a T_c exceeding nitrogen boiling temperature.[4][5]

[1] A. P. Drozdov, et al., Nature 525, 73 (2015). D. Duan, et al., Scientific Reports 4, 6968 (2014)
[2] N. Ashcroft, Phys. Rev. Lett. 92, 187002 (2004)
[3] N. Bernstein, et al. Phys. Rev. B 91, 060511(R) (2015); J.A. Flores-Livas et al., cond-mat/1501.06336; R. Akashi, et al., Phys. Rev. B 91, 224513 (2015).I. Errea, et al., Phys. Rev. Lett. 114, 157004 (2015)
[4] A. P. Drozdov, M.I. Eremets and I.A. Troyan, cond-mat/1508.06224 (2015)
[5] C. Heil and L. Boeri, Phys. Rev. B 92, 06508 (R)(2015); J. A. Flores-Livas, M. Amsler, C. Heil, A. Sanna, L. Boeri, G. Profeta, C. Wolverton, S. Goedecker, E. K. U. Gross, http://de.arxiv.org/abs/1512.02132

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Ultrafast Dynamics of Excited Electrons in Materials

Marco Bernardi

How does an excited electron lose its energy? This problem is central in fields ranging from condensed matter physics to electrical engineering and energy. The talk will discuss first-principles calculations of the ultrafast (sub-ps) dynamics of out-of-equilibrium charge carriers in semiconductors and metals [1–3]. Carrier dynamics on longer (ps-ns) time scale, as induced by radiative [4] and non-radiative recombination, will also be discussed. We will focus on calculations of electron-phonon, electron-electron, electron-defect, and electron-photon scattering that can predict the relaxation time, mean free path, and lifetime of excited carriers in materials. This framework is applied to case studies of relevance in optoelectronics and renewable energy. The talk will close with a summary of the strategies challenges to compute electron dynamics from first principles.

M. Bernardi et al., Phys. Rev.Lett. 112, 257402 (2014)
M. Bernardi et al., PNAS. 112, 5291 (2015)
M. Bernardi et al., Nature Commun. 6:7044 (2015)
M. Palummo, M. Bernardi, and J. C. Grossman, Nano Lett. 15, 2794 (2015)

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Ultrafast charge separation dynamics in photovoltaic heterojunctions

Carlo Andrea Rozzi, Elisa Molinari, Angel Rubio, Giulio Cerullo, Christoph Lienau

The photoinduced charge-separation events occurring in photovoltaic and light harvesting systems have traditionally been interpreted in terms of the incoherent kinetics of optical excitations and of charge hopping. Although signatures of quantum coherence were recently observed in energy transfer in photosynthetic bacteria and algae [1] still very little is known about the role of quantum coherence at room temperature in technologically relevant organic photovoltaic materials. Recent experiments found evidence for an ultrafast long-range charge separation in such systems but could not differentiate between coherent and incoherent charge-transfer models.[2] By combining TDDFT simulations of the quantum dynamics and high time resolution femtosecond spectroscopy, we provide evidence that the coherent coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer both in covalently bonded molecules [2] and in non-bonded bulk heterojunctions [3]. We have exploited the results of our research to design, syntesize and characterize a novel molecular scaffold for photovoltaic applications.[4]

G. S. Engel et al. Nature 446, 782-786 (2007)
S. Gélinas et al., Science 343, 512–516 (2014)
C. A. Rozzi et al., Nat. Comm 4, 1602 (2013)
S. M. Falke et al., Science 344, 1001 (2014)
S. Pittalis et al., Adv. Func. Mat. (2014)

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Coupled Electron-Nuclear Dynamics in Non-Adiabatic Processes

Federica Agostini

The Born-Oppenheimer (BO) approximation is widely employed to account for the coupling between electrons and nuclei when describing dynamical processes in molecular systems. It relies on the assumption that the typical time-scales of electronic and nuclear motion in a molecule are adiabatically separable. This hypothesis allows to write the full electron-nuclear wave function as a single product of an electronic eigenstate, for each fixed nuclear configuration, and a time-dependent nuclear wave function. Such an approximation is fundamental for our understanding of molecular processes. However, it is not suited when non-adiabatic effects due the coupling between the nuclear motion and excited electronic states become important, which are essential to understand phenomena such as vision, photovoltaic processes and Joule heating in molecular junctions.

The talk will show how the BO approximation can be made exact [1], by preserving the single product form of the full electron-nuclear wave function and accounting for electronic excitations. This exact factorization approach will be introduced and used as a tool [2] to interpret non-adiabatic processes beyond Ehrenfest dynamics [3], i.e. the uncorrelated product Anstatz for the electron-nuclear molecular wave function. Furthermore, algorithms will be derived [4, 5] to describe electronic non-adiabatic processes employing a description of nuclear dynamics in terms of classical trajectories. Applications [4, 5] to model systems and to small molecules will be presented to numerically validate such quantum-classical scheme.

[1] A. Abedi, N. T. Maitra and E. K. U. Gross, Phys. Rev. Lett., 105, 123002 (2010).
[2] A. Abedi, F. Agostini, Y. Suzuki and E. K. U. Gross, Phys. Rev. Lett., 110, 263001 (2013).
[3] F. Agostini, A. Abedi, Y. Suzuki, S. K. Min, N. T. Maitra and E. K. U. Gross, J. Chem. Phys., 142, 084303 (2015).
[4] F. Agostini, A. Abedi and E. K. U. Gross, J. Chem. Phys., 141, 241101 (2014).
[5] S. K. Min, F. Agostini and E. K. U. Gross, Phys. Rev. Lett., 115, 073001 (2015).

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GW and molecules: a benchmark for G0W0 and developments beyond.

Michiel van Setten

In the first part of this presentation the GW100 benchmark set for G0W0 applied to molecular systems will be presented. It is a collaborative effort between the developers of the GW parts of TURBOMOLE, FHI-AIMS and BerkeleyGW establishing a well tested and converged set of benchmark results. Different basis-sets, frequency methods and core/valence treatments are compared. In the second part we move beyond G0W0. Various levels of self-consistency, foGW, GfoW0, and qsGW, are compared to reference CCSD(T) results and to each other. It is shown that qsGW is indeed completely independent of the starting point and that the two partial self-consistency approaches come close if the optimal starting point is used. Finally we explore in another direction discussing developments to take into account spin-orbit effects in a two-component extension of the G0W0 framework.

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Improved quasiparticle wave functions and mean field for G0W0 calculations

Manish Jain

The first-principles GW method [1] is an interacting many-body Green's function method for ab initio calculations of the quasiparticle energies. This method has been shown to work extremely well for calculating spectroscopic properties for a wide variety of condensed matter systems -- metals, semiconductors and insulators, and nanostructures. In its standard formulation [1], the self energy operator is taken to be diagonal in the density functional theory (DFT) Kohn-Sham basis within the G0W0. However, there are known situations in which this diagonal G0W0 approximation starting from DFT is inadequate. We present two schemes [2] to resolve such problems. The first, which we called sc-COHSEX+GW, involves construction of an improved mean field using the static limit of GW, known as COHSEX (Coulomb hole and screened exchange), which is significantly simpler to treat than GW. In this scheme, frequency-dependent self energy is constructed and taken to be diagonal in the COHSEX orbitals after the system is solved self-consistently within this formalism. The second method is called off diagonal-COHSEX GW (od-COHSEX+GW). In this method, one does not self-consistently change the mean-field starting point but diagonalizes the COHSEX Hamiltonian within the Kohn-Sham basis to obtain quasiparticle wave functions and uses the resulting orbitals to construct the GW self energy in the diagonal form. We apply both methods to a molecular system, silane, and to two bulk systems, Si and Ge under pressure. Our results show that these methods give good quasiparticle wavefunctions and can solve the qualitatively incorrect DFT mean-field starting point.

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Stochastic Approaches to Electronic Structure: From DFT and TDDFT to GW and BSE

Eran Rabani

In this talk, I will summarize our work on stochastic electronic structure methods for DFT, TDDFT GW and BSE, which rely on novel theoretical concepts such as stochastic orbitals, stochastic traces, stochastic time-dependent propagation, stochastic matrix compression and stochastic decoupling techniques. Beyond the theoretical interest, the formalism enables sub-linear scaling for DFT and TDDFT, nearly linear scaling for GW (breaking the theoretical scaling limit), and quadratic scaling for BSE. Applications for silicon and CdSe nanocrystals will be discussed.

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Total energy calculations beyond the Random Phase Approximation

Thomas Olsen, Kristian Thygesen

The Random Phase Approximations (RPA) comprises an accurate method for obtaining binding energies in van der Waals bonded systems from first principles. However, the method suffers from self-correlation errors on the order of 0.5 eV per electron and performs badly for covalent interactions. First, we will remedy this in the context of time-dependent density functional theory, where the bare Coulomb interaction is augmented by an exchange-correlation kernel. It will be shown that standard adiabatic kernels break down and a parameter-free renormalization scheme is introduced that renders the interacting response function well-behaved and significantly improves the accuracy of RPA. Second, RPA is extended within many-body perturbation theory by including electron-hole interactions in the irreducible response function. In particular, ground state energies obtained from the Bethe-Salpeter equation, are shown to give an accurate account of strong electronic correlation in dissociating molecules.

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Dielectric matrix formulation of correlation energies in the Random Phase Approximation: Inclusion of exchange effects

DarRoccaio Rocca, Bastien Mussard, Georg Jansen, Janos Angyan

Starting from the general expression for the ground state correlation energy in the adiabatic connection fluctuation dissipation theorem (ACFDT) framework, it is shown that the dielectric matrix formulation, which is usually applied to calculate the direct random phase approximation (dRPA) correlation energy, can be used for alternative RPA expressions including exchange effects [1]. Within this framework, the ACFDT analog of the second order screened exchange (SOSEX) approximation leads to a logarithmic formula for the correlation energy similar to the direct RPA expression. Alternatively, the contribution of the exchange can be included in the kernel used to evaluate the response functions. In this case the use of an approximate kernel is crucial to simplify the formalism and to obtain a correlation energy in logarithmic form. Through the use of a compact auxiliary basis set, this dielectric matrix-based formalism can be efficiently implemented both in localized and plane-wave basis sets [1-3]. A series of test calculations on atomic and molecular systems shows that exchange effects are instrumental to improve over direct RPA results.

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A unified approach to reactions in gas phase and solution via topological coordinates

Fabio Pietrucci, Marco Saitta

Ab initio molecular dynamics, in combination with techniques that enhance the sampling of rare events, is a powerful tool to explore the mechanisms, thermodynamics and kinetics of activated processes. However, so far it has been impossible to embark on a systematic and wide-range study of chemical reaction dynamics in solution because suitable general-purpose reaction coordinates were missing. Graph theory – the toolbox behind Google's PageRank algorithm – offers a possible solution: capturing the topology of a network of atoms starting from the matrix of chemical bonds. We recently introduced a new class of collective variables able to track different reaction mechanisms without fine tuning. Our approach is flexible enough to discover multiple pathways and intermediates starting from minimal insight, and it allows passing in a seamless way from reactions in gas phase to reactions in liquid phase, with the solvent active role fully taken into account. In the complex scenario of prebiotic reaction networks, we obtained crucial new insight into the interplay of the different formamide reaction channels and on solvent and temperature effects on pathways and barriers.

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Calculating the pressure-temperature phase diagrams of materials

Robert Baldock, University of Cambridge, Lívia Pártay, University of Cambridge, Albert Bartók, University of Cambridge, Michael Payne, University of Cambridge, Gábor Csányi, University of Cambridge

We extend the Nested Sampling algorithm to simulate materials under periodic boundary and constant pressure conditions, and show how it can be efficiently used to determine the phase diagram directly from the potential energy in a highly automated fashion. The only inputs required are the composition and the desired pressure and temperature ranges. In particular, solid-solid phase transitions are recovered without any a priori knowledge about the structures of solid phases. After benchmarking the algorithm on the Lennard-Jones system, we apply the algorithm to aluminium and the NiTi shape memory alloy.

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Layered iridates: a discussion on noncollinear vs collinear treatment of 5d electron systems

Victor Pardo

Layered iridates have drawn intense attention recently, mainly because of the prediction of different types of topologically non trivial phases in iridate-based nanostructures [1,2], and also because of the possible appearance of superconductivity in Sr_2IrO_4 has been suggested [3].

In this talk, I will focus on compounds containing Ir^{4+}:d^5 cation in an octahedral coordination, i.e. one-t_{2g}-hole systems. These are frequently described as j_{eff} = 1/2 states and comparisons with the one-e_g-hole in cuprates have often appeared in literature, particularly for the case of a square lattice with antiferromagnetic correlations.

I will discuss how one can obtain somewhat contradictory results for the electronic structure properties of this kind of iridates when utilizing different schemes for calculating the band structure of the system. We will describe how close Sr_2IrO_4 is to being a pure j_{eff} = 1/2 state and what are the requirements for obtaining that solution within DFT techniques. Also, what the implications of these are in terms of comparing with available experiments.

The main conclusion we obtained from our calculations [4] is that standard collinear calculations are not sufficient to capture the electronic structure of this kind of correlated 5d electron systems and that only when noncollinear magnetism is set on, a solution close to the single-ion picture of a j_{eff} = 1/2 state can be obtained.

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Using the electrochemical dimension for modelling surface and interfaces for energy materials

J.-S. Filhol, N. Lespes, M.-L. Doublet

The electrochemical interface is fundamental to understand electrochemical reactions either for electrocatalysis applications (fuel cells), corrosion, electroplating or for electrochemical energy storages such as Li-ion batteries. Nevertheless, it is extremely difficult to model not only because of the occurring electrochemical effects but also because of the complexity of the electrode-solvent interface. Classical models fairly well reproduce the behavior of such an interface by introducing more or less complex description of the electric double layer (Helmholtz plane, diffuse layer etc.), but are oblivious to the quantum phenomena occurring at the interface. Ab initio approaches can describe this quantum behavior with good accuracy; nevertheless most of these approaches are not accounting for the full complexity of the electrochemical interface as it would necessitate including the solvent (at least hundreds/thousands of molecules) and electrolyte (with their interaction with the solvent and the surface) in their structural and time-dependent dimension leading to unmanageable calculations. We will present the general electrochemical approach and formalism at DFT level including an implicit solvent approach (exemplified by a Li/Ethylene carbonate (EC) interface) that allows recovering the proper electrochemical properties such as surface capacitance at a limited cost. We will highlight the electronic and structural effects that modify the interface reactivity. We will in particular discuss how implicit/explicit model should be used in order to recover the potential stability for Li-electrodes in carbonate solvents and how the electrode growth or consumption are linked with the local chemical/electrochemical parameters. Finally, we will show, using the Fukui function tool previously developed, that the redox species involved in the reduction of Li+ includes the first solvation sphere possibly explaining why solvent molecules can break at the interface.

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Poster contributions

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Rattler modes in A_8Sn_{46-x} (x =0,2) clathrates

Peter O. Egbele, Daniel P. Joubert

Direct comparison of vibrational modes between three different members of binary type-I Sn Clathrates (A = Cs, Rb, K) with experiments is presented. Our calculated spectrum is in reasonable agreement with the Raman data. We are able to identify the low-frequency “rattling” vibrational modes in these materials, which are due to the motion of the guest atoms that are loosely bound in the Sn cages. We have also addressed the role of Sn vacancies in the dynamics of the framework and answer the question: do the guest atoms in the vacancy structure rattle?

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Surfaces of the Al_5Co_2 complex intermetallic compound : from structure to chemical reactivity

M. Meier, J. Ledieu, M.-C. De Weerd, V. Fournée, É. Gaudry

Recent advances in heterogeneous hydrogenation catalysis have identified few Al-Co complex intermetallic compounds as promising candidates for the development of efficient cheap catalytic materials [1]. The performances of these catalysts have been ascribed to their specific surface structure, made of small, stable, and well-separated atomic ensembles containing generally a unique active transition-metal element. To elucidate the reactivity of the Al-Co complex intermetallic catalysts, an investigation at the atomic scale is mandatory. Here, we focus on the low-index surfaces of Al_5Co_2 ($P6_3/mmc$, a = b = 7.67 Å, c = 7.61 Å). Three low-index surfaces - (001), (100) and (210) - are investigated by an approach combining both surface science techniques under ultra-high vacuum and calculations based on density functional theory. In all cases, the surface terminates at specific bulk layers where various fractions of specific sets of Al atoms are missing, leading to different surface reconstructions, also depending on the surface preparation conditions [2]. Such reconstructions are not usual in the case of metallic surfaces. They are related to the specific chemical bonding network present in Al_5Co_2. The reactivity and selectivity of these surfaces towards the semi-hydrogenation of acetylene are then discussed in light of the results published on the related compound $Al_{13}Co_4$ [3,4].

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Lattice dynamics and electron-phonon coupling calculations using nondiagonal supercells

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We study the direct calculation of total energy derivatives for lattice dynamics and electron-phonon coupling calculations using supercell matrices with nonzero off-diagonal elements. We show that it is possible to determine the response of a periodic system to a perturbation characterized by a wave vector with reduced fractional coordinates (m_1/n_1, m_2/n_2, m_3/n_3) using a supercell containing a number of primitive cells equal to the least common multiple of n_1, n_2, and n_3. If only diagonal supercell matrices are used, a supercell containing $n_1n_2n_3$ primitive cells is required. We demonstrate that the use of non-diagonal supercells reduces by over an order of magnitude the computational cost of obtaining converged zero-point energies and phonon dispersions for diamond and graphite. We also perform electron-phonon coupling calculations using the direct method to sample the vibrational Brillouin zone with grids of unprecedented size, which enables us to investigate the convergence of the zero-point renormalization to the thermal and optical band gaps of diamond.

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Theoretical Model for the Spin-Dependent Seebeck Coefficient of InSb

Nicholas A. Pike, Jose Alonso Miranda Sanchez, Marco Di Gennaro, Matthieu J Verstraete

The surprisingly large Seebeck coefficient in Indium Antimonide could lead to a diverse array of thermoelectric applications for InSb. Our recent work [1] in calculating the transport properties of InSb in a magnetic field showed oscillations of the thermopower as a function of the inverse magnetic field and a large peak in the spin-dependent Seebeck coefficient, in reasonable agreement with recent experimental work [2]. We now extend our calculation to additional scattering mechanisms to better analyse the physical nature of the large Seebeck Coefficient observed by Jaworski, et al.

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Effect of vertex corrections in Hedin's equations for predicting bandgaps in solids

Per S. Schmidt, Kristian S. Thygesen

The first-principles application of many-body perturbation theory at the level of Hedin's GW approximation [1] to the calculation of energy levels in semiconductors and insulators has proved to yield values in good agreement with experiments. In spite of this, the justification of neglecting vertex corrections in the self-energy is not obvious. In this work we improve upon the widely used G0W0 approximation for the self-energy by including these vertex corrections in both the screened Coulomb interaction, W, and the self-energy. The vertex is approximated through two different kernels and compared, a renormalized adiabatic LDA kernel (rALDA [2]) and a jellium-with-gap kernel (JGMsx [3]). Standard G0W0 calculations systematically underestimate bandgaps and we show that the vertex corrections results in increased bandgaps of solids, bringing them closer to experimental values. In addition to being more accurate, the calculations are also shown to converge faster with respect to basis set size. The effect of including vertex corrections only in W has also been investigated. The computational cost is similar but the resulting bandgaps decreased in size, and are thus further away from experimental values.

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Reduced density-matrix functional theory via a wave-function based approach

Robert Schade, Peter Bloechl, Thomas Pruschke

We propose a new method for the calculation of the electronic and atomic structure of correlated electron systems based on reduced density matrix functional theory (rDMFT). The density matrix functional is evaluated on the fly using Levy's constrained search formalism. The present implementation rests on a local approximation of the interaction reminiscent to that of dynamical mean field theory (DMFT). This wave function based approach can be integrated into the existing DFT framework by making use of natural orbitals.

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First principles study of valence and structural transitions in rare earth compounds under pressure

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The self-interaction corrected (SIC) local spin-density (LSD) approximation is used to study the ground state valency configuration of the rare earth mono-chalcogenides (RX) and the changes in electronic structure that occur under pressure. It emerges that at ambient conditions all the RX are stabilized in the NaCl structure, but that under pressure a number of them undergo a succession of structural (NaCl to CsCl) and valence (2+ to 3+) transitions, the order of which is determined by the degree of f-electron localization. This interplay between structural and electronic degrees of freedom becomes especially noticeable in EuO, where we predict reentrant valence behaviour in line with recent pressure experiments.

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Improving anharmonic vibrational calculations from first principles

Joseph C.A. Prentice, Bartomeu Monserrat, Richard J. Needs

The vibrational self-consistent field (VSCF) method, as described in Ref. [1], has had several successes in accurately calculating the anharmonic properties of various materials, such as diamond [1], ice [2] and solid hydrogen [3]. However, a practical issue with the method is the large number of DFT calculations required to map the Born-Oppenheimer energy surface sufficiently accurately. We look at improvements to the method that reduce this computational load, in particular using data on forces from DFT calculations to improve the accuracy of the mapping. Results using this improved method are presented for competing structures of silicate perovskite ($CaSiO_3$) under lower mantle conditions. Further improvements, involving the inclusion of n-body coupling between phonons, and their possible implementation are also discussed.

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Ab initio predictions of structure preferences and band gap character in ordered $AlAs_{1-x}Bi_x$ alloys

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In this work, we have studied a mixed III-V semiconductors of the Al(As,Bi) composition. We have calculated a number of ordered structures of this composition in a series of first-principles calculations within density functional theory, making use of the full-potential linearized augmented plane-wave method as implemented in the WIEN2k code. The calculations have been done for "minimal" supercells realizing the 1:3, 1:1, and 3:1 relations of As:Bi at the anion sublattice. Specifically, the CuAu and chalcopyrite structures were considered for the 1:1 relation; the famatinite and luzonite structures for the 1:3. In all cases, the full structure optimization has been performed with spin-orbit interaction taken into account, and the band structure/band gap analysis done. As expected, an insertion of Bi into the AlAs enlarges, on average, the cell volume and results in marked disparity of the bond lengths. The optical band gap decreases with Bi composition; the indirect to direct band gap crossover is interpolated to happen at nearly 16% of Bi. The spin-orbit splitting increases with Bi compositions, and exceeds the band gap starting from a Bi composition of about 50%. The study is concluded by a report on calculated optical properties, i.e., the dielectric function and refractive index, for different Bi compositions.

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Role of van der Waals interactions in the adsorption of CH_3 and C_6H_6 on α-Cr_2O_3, α-Fe_2O_3 and α-Al_2O_3 surfaces

Samira Dabaghmanesh, Bart Partoens, Erik Neyts

Van der Waals (vdW) interactions play an important role in the adsorption of atoms and molecules on the surface of solids. This role becomes more significant whenever the interaction between the adsorbate and surface is physisorption. Thanks to the recent developments in density functional theory (DFT), we are now able to employ different vdW methods. This helps us to account for the long-range vdW forces which are absent in popular DFT exchange correlation functionals. However, the choice of the most efficient vdW functional for different materials is still a remaining question.
In our work, we examined different vdW approaches (i.e. vdW-DF [1], vdW-DF2 [2], optPBE-vdW, optB88-vdW, optB86b-vdW[3], and the vdW method of Grimme [4] in the form of DFT-D2, DFT-D3, and DFT-D3-BJ) to compute bulk and molecular adsorption properties of M_2O_3, (M: Cr, Fe, and Al) as the well-known example of corundum family. For the bulk properties, we compared our results for the heat of formation, cohesive energy, lattice parameters and bond distances between the different vdW functionals and available experimental data. Next we computed the adsorption energies of the benzene molecule (as an example of physisorption) and CH_3 (as an example of chemisorption) on top of the (0001) M-terminated and MO-terminated surfaces. We compared the adsorption energies obtained using vdW corrections with those obtained using the PBE functional. We found that the vdW functionals play important role not just in the weak adsorptions but even in strong adsorption.

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Ordered growth of metal nanoparticles on supported graphene: insights from ab-initio calculations

Fatema Mohamed, Marco Pividori

For most practical applications, metal nanoparticles (NPs) need to be supported on a substrate that can act as a deposition template for growing them in regular arrays. This prevents sintering at high temperatures, a process that would deactivate the catalytic devices. The Moiré pattern due to the small lattice mismatch between graphene and Ir(111) works as an efficient template for the ordered growth of some transition metal NPs. With the help of ab-initio calculations performed for adsorption of monomers and small clusters of Cu, Pt, and Ir, we explain the behaviour of different metals, predicting results in agreement with the available experimental findings and identifying the criteria for the suitability of a metal to form ordered nanocluster arrays. Moreover, preliminary results indicate that even materials that do not form cluster superlattices can be grown through the application of cluster seeding using properly chosen metals.

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First-principles atomistic simulations of defects in epitaxial graphene on Ni(111)

Virginia Carnevali, Gianluca Prandini

The analysis of unprecedented high-resolution scanning tunneling microscopy (STM) images of graphene/Ni(111) shows the presence of different types of defects, mainly due to carbon vacancies and partially filled with trapped Ni adatoms. We have proposed some structural models and verified their reliability on the basis of the energetics and the comparison between observed and simulated STM images, obtained from ab-initio density functional theory calculations. In particular, we have studied in details a triple-vacancy defect with one Ni atom trapped inside, that shows a peculiar dynamical behavior in the interaction with carbon monoxide. We have investigated and characterized also other defects, even more extended, extracting some general trend to predict their stability and their abundance. Preliminary results concerning their activity under the exposure of small molecules of environmental importance have been also obtained.

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Soft Norm Conserving Accurate Pseudopotentials

Santanu Saha, Stefan Goedecker

Soft and accurate pseudopotentials are necessary for efficient electronic structure calculations. Adding non-linear core correction (NLCC) along with semi-core states to the Goedecker type pseudopotentials [1],[2] and optimizing the shape of the orbitals, we generated soft norm conserving pseudopotentials for the Perdew, Burke, Ernzerhof (PBE) [3] functional for the elements in the first three periods of the periodic table. They are also accurate with an average delta value of less than 0.1 meV/atom in Delta Test [4]. During the construction of the pseudopotential, all possible excited states along with the ground state of the atom are considered and hence it is transferable by construction. Benchmarking against the G2-1 test set, we obtain average atomization energy error of 1.32 KCal/mol. The all-electron energies were obtained using the aug-cc-pV5Z Gaussian basis set.

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Unbiased potential energy surface search for MnC_{60} (M = Li, Na, K, Ca, Al, Mg, Be, Si)

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It is very diffcult to predict the stable configuration of a fullerene with M metal atoms, M_nC_{60} (M = Li, Na, K, Ca, Al, Mg, Be, Si and n =1-6,8 ,12, 20, 32) due to the huge number of possible structures. Several theoretical investigations were carried out previously on the interaction between metal/alkaline metals on C_{60} [1,2,3,4,5]. All of the previous investigations were based on biased structure prediction methods and they do not agree on the number of atoms required for the transition from wetting to cluster formation. We have employed an unbiased structure prediction method at the density functional theory (DFT) level to explore different stable configurations of MnC_{60}. It is observed that ionic interaction between C_{60} and alkaline atoms is strong untill the number n of atoms on C_{60} reaches 6 for Na, K and 12 for Li. As n becomes larger, metallic bonding becomes stronger and alkaline atoms start to form a droplet. Ca gets homogeneously distributed over C_{60} when n=32, forming a core/shell kind of structure. Si strongly binds with C_{60} but if we increase the number of Si atom more than 2, they start to form droplets. Mg and Be atom bind weakly to C_{60} and cannot be wetted with any n. On the other hand, adsorption property changes if n>1 for Al. In summary, our study shows that among all the alkali, earth alkali and metals, only few elements can form a homogeneous coverage of C_{60} and that this is only possible for certain magic numbers which are element dependent.

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Ab-initio Studies of Phase Transitions and Defects in Solids

Thomas Gruber, Felix Hummel, Theodoros Tsatsoulis, Andreas Grüneis

We present recent progress in the application of quantum chemical wavefunction based methods to the study of solid state systems. The employed ab-initio methods include Moller-Plesset perturbation and coupled-cluster theories. We study pressure driven solid-solid phase transitions in LiH and carbon allotropes as well as the Schottky defect formation energy in MgO. The obtained results allow for the benchmarking of approximate density functionals and illustrate the scope of our computer code implementations.

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Optoelectronic properties of Chrome yellow pigments $PbCr_{1-x}S_xO_4$: Density Functional Theory calculations and electrochemical measurements

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Chrome yellow refers to a group of synthetic inorganic pigments that became popular as an artist's material from the second quarter of the 19th century and is often encountered in oil paintings such as those by Vincent van Gogh. The color of the pigment is related to its chemical composition ($PbCr_{1-x}S_xO_4$ with $0 \leq x \leq 0.8$) and crystalline structure. Their shades range from the yellow-orange to the pale-yellow tones with increasing amount of sulfur. We observe that orthorhombic sulfur-rich $PbCr_{1-x}S_xO_4$ solid solutions ($x>0.4$) are more prone towards photo-reduction than sulfur-free monoclinic $PbCrO_4$. Complementary to the measurements, we report the results of density functional theory calculations of the electronic, and optical properties of $PbCr_{1-x}S_xO_4$ solid solutions with $0 \leq x \leq 0.8$. The ground state structures of $PbCrO_4$ and $PbSO_4$, monoclinic and orthorhombic respectively, are considered in the calculations of all studied pigments. Calculations of the conduction and valence band alignment show a decrease in the position of the valence band maximum and consequently a decrease in p-type dopability for increasing sulfur concentrations. Increasing the sulfur amount also yields a blue shift in the band gap. This shift explains the color range of the chrome pigments and can be understood from a smaller contribution of Crd orbitals to the bottom of the conduction band. Although there is less photon absorption in sulfur-rich pigments, lower reflectivity for such solid solutions results in a higher photocurrent compared with sulfur-free $PbCrO_4$. This work for the first time explores the electronic structure and optical properties of sulfur-doped chrome yellow pigments at ambient pressure.

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Calculating forces in the random phase approximation for solids

Benjamin Ramberger, Georg Kresse

Recent progress in the application of the random phase approximation (RPA) to solid systems made RPA-correlation energies readily accessible by computational means, even for large systems. However, there is not yet an efficient way to calculate forces in the RPA within the current framework. Since the calculation of forces is crucial for the simulation of elastic and vibrational properties as well as for structure relaxations, this is a promising area for further investigation. In this work, analytical expressions that allow an efficient numerical calculation of forces within the RPA are presented in terms of Green's functions. The new method was tested on diamond C and first results support the proposed expressions.

http://othes.univie.ac.at/37990/

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Towards Efficient Coupled Cluster Theories for Solids

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Wave function based methods such as Coupled Cluster theories allow for very accurate solutions to the many-electron Schrödinger equation. The main advantage of wave function based methods is their ability to obtain systematic approximations to the exact many-electron correlation energy, albeit at a relatively large computational cost. This is in sharp contrast to approximate density functionals and Green's function based methods. In this work we discuss methods to reduce the computational cost of wave function based methods including explicit correlation, efficient one-electron basis sets and tensor rank decomposition techniques. These techniques have the potential to reduce both, the scaling of the computational cost with respect to the system size as well as the prefactor of the computational cost.

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Electronic and vibrational properties of $TiSe_2$ in the charge-density wave phase from first principles

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The charge-density wave instability in $TiSe_2$ has recently received considerable attentions, both for conceptual reasons and technological applications, since in this system the charge-density wave phase competes with superconductivity and its origin remains controversial. In fact, several mechanisms have been proposed for this structural transition depending on the driving role played either by the electron-electron or by the electron-lattice interaction [1-4]. We present a study of the charge-density wave instability in $TiSe_2$ from first principles calculations. We consider several local functionals and both experimental and theoretical cell parameters. We show that, if the cell parameters used are in agreement with the experiment, density functional calculations are able to reproduce not only the structural instability of $TiSe_2$ but also the effective distortion observed in the experiments. The results obtained are robust with respect to the local functional used. We also study the electronic structure evolution of the system under the charge-density wave deformation. In particular, we apply the unfolding technique in order to compare the calculated energy bands for the distorted structure with angle-resolved photoemission spectroscopy (ARPES) data taken at low temperature. In order to obtain a better agreement between ARPES and calculated bands, we investigate the effect of the correlation on the electrons of the localized Ti-d orbitals by using the LDA+U method. We show that, within this approximation, the electronic bands for both the undistorted and distorted structure are in very good agreement with ARPES. On the other hand, the U eliminates the phonon instability of the system. Some possible explanations for this counter intuitive result are proposed.

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Exchange and correlation effects on the universal increase in the superconducting critical temperature of two-dimensional semiconductors at low doping

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The superconducting temperature of two-dimensional multivalley semiconductors is enhanced at low doping. It has recently been shown that this enhancement is linked to the electron-electron interaction enhancing the response to a perturbation inducing the valley polarization that can be due to the electron-phonon coupling [1]. In this work, we extend this study to analyze the exchange and correlation effects on the electronic, magnetic, and vibrational properties of Li-doped ZrNCl and show that these properties can be calculated by ab initio density functional theory only by using approximations beyond the generalized gradient approximation. Finally, we present the link between the enhancement of the spin susceptibility and superconducting temperature by demonstrating that the electron-phonon coupling is acting as a pseudo-magnetic field causing the valley polarization [2].

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MP2 exchange energy of large systems

Tobias Schäfer, Georg Kresse

A standard approach of quantum chemistry is to evaluate the energy of matter using Hartree-Fock theory and the correlation energy in second order using Moeller-Plesset perturbation theory (MP2). This approach is however rather costly, since conventional MP2 implementations scale with roughly the fifth power of the number of electrons (N^5). Here we explore two methods to reduce the scaling. Both are based on the Laplace transformation, or equivalently a description of perturbation theory in imaginary time [1]. The first algorithm calculates the one-particle Green's function (N^3) and then evaluates the second order diagrams by a Monte-Carlo integration.[2] The second algorithm uses a trick commonly applied in quantum information theory, the so called Schmidt decomposition, and allows to evaluate the MP2 energy with a complexity proportional to N^4. Although not discussed here in detail, similar algorithms allow to calculate second order screened exchange as well as the particle-hole ladder diagrams with a similar low complexity.

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The Quantum Thermal Bath: a semi-classical approach to nuclear quantum effects

Yael Bronstein, Philippe Depondt, Fabio Finocchi

In the recent past, increasing interest has risen for nuclear quantum effects (NQE), especially in hydrogen-containing systems. Indeed, NQE such as proton tunneling and zero-point energy often play a crucial role in the properties of these materials, even at room temperature. The standard methods to simulate NQE are based on path integrals. However, an interesting alternative to these methods is the Quantum Thermal Bath [1] (QTB) which consists in a semi-classical approach that provides exact response functions for harmonic oscillators. We can show through simple models that the QTB is a viable approach to take into account NQE even in anharmonic systems, at a relatively low computational cost, beyond the inherent limitations of its semi-classical aspect. Hence, the QTB enables realistic simulations of complex systems, generating static and dynamic information, such as pair correlation functions and vibrational spectra, which can be directly confronted with experimental results. Relying on recent works [2,3,4], we show that this method is particularly successful in the study of the symmetrization of hydrogen bonds in several systems. Indeed, the difficulty resides in the identification of a precise transition pressure since the phase transition is often blurred by quantum or thermal fluctuations. It can depend on the oxygen-oxygen distance, as in high-pressure ice [2], but it can be affected by the electric field induced by ionic impurities [3] or by the inherent asymmetric environment of the hydrogen bonds, as in the delta phase of AlOOH [4]. The QTB is based on a Langevin-type equation for the nuclei where the random white noise has been replaced by a “colored” noise [1], making the comparison with results from simulations that treat nuclei as classical particles quite straightforward. In the different cases studied here, the QTB provides a quite precise transition pressure (from 10 GPa in AlOOH to 90 GPa approximately in salty ices). Moreover, by comparing results from QTB and standard ab initio molecular dynamics, we are also able to disentangle the respective roles of NQE and thermal fluctuations in phase transitions that imply hydrogen-bond symmetrization. Finally, we extract from our simulations simple models based on effective potentials for the protons that enable us to better understand the mechanisms underlying these phase transitions.

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Local density fitting within a Gaussian and plane waves approach

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The computationally most expensive step in the construction of the Kohn-Sham (KS) matrix is the evaluation of the Coulomb matrix. The latter requires the calculation of two-electron integrals with the characteristic $O(N^4)$ problem. Baerends et al. [1] introduced a local resolution of identity approach (LRI), where the atomic pair densities are approximated by an expansion in one-center fit functions reducing the scaling order to $O(N^3)$.

In this work, the LRI technique was adapted for usage in a Gaussian and plane waves (GPW) approach and implemented in the CP2K program [2,3] package. The fitted density is employed for evaluation of Coulomb as well as exchange-correlation potential. The construction of the KS matrix in GPW scales already linearly with respect to system size since the plane wave expansion of the density is exploited to solve the Poisson equation in Fourier space. The combination of a local basis and an auxiliary basis set of plane waves leads to an O(N) process for the evaluation of the Coulomb matrix. Using LRI, improvements are obtained for the calculation of the grid-dependent terms. The prefactor for building the KS matrix is reduced resulting in a system-dependent speed-up. Furthermore, the scalability of the grid-based calculation and integration of the potential with respect to number of CPUs are be simplified and improved. Results regarding timings and scalability are presented for liquid water and ice XV demonstrating that a speed-up of the SCF step by a factor of at least three can be expected for large and medium-sized systems. The accuracy of the LRI approach is assessed by reaction energies and structural properties for a broad range of systems.

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Spin-unrestricted MP2 forces for condensed phase simulations

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We report the first massively-parallel implementation of analytical spin-unrestricted MP2 (UMP2) forces in CP2K program [1]. It is an extension of the previous work on spin-restricted MP2 forces [2] based on resolution-of-identity Gaussian and Plane Waves (RIGPW) approach for calculation of four-center Coulomb integrals. On thousands of processor cores it is possible to calculate energy UMP2 energy and forces in minutes, dozens of minutes and several hours for systems containing less than 100 , 100-200 and more than 200 second-row atoms respectively using triple-zeta quality Gaussian basis sets. The UMP2 forces are ca. 3 times computationally more expensive than the RMP2 ones, however, the former exhibit a better parallel scaling. The code has been successfully applied to cell optimization of molecular crystal of TEMPO radical, as well as to study geometry relaxation, formation energy and spin density distribution of F-center in lithium fluoride.

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First-principles calculations on the interplay between O adatom and the charge density wave in indium nanowires on Si(111)

Jung-Min Hyun, Geunseop Lee, Hanchul Kim

Metal adsorbed semiconductors have attracted much interest in surface science because they provide useful platforms to study low-dimensional phenomena including phase transition. In nanowires self-assembled on the Si(111) surface undergo phase transition from room-temperature (RT) 4×1 to low-temperature 8×2 structure at ~120K, which is known to be a charge density wave (CDW) condensation. O adatoms are known to increase the critical temperature (Tc) while other adsorbates such as H, Na, or In adatoms are decrease Tc [1,2]. In this presentation, we have investigated the interaction between oxygen impurities and the CDW. We found that the adsorbed O favors the interstitial site between the In nanowires and the Si substrate to the surface adsorption claimed in previous calculations [3,4]. A few stable interstitial adsorption structures were found and their scanning tunneling microscopy (STM) images were simulated and compared with the experimental STM images to identify the observed O-induced defect features. Based on these results, the interplay between the O adsorption structures and the CDW will be discussed.

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Energetics and STM image simulation of Gd doped topological insulator, Bi_2Te_3

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Topological insulators (TI) have metallic surface state in contrast to the insulating bulk state [1], and the magnetic impurities are predicted to open an energy gap in the metallic surface state.Recently, Gd doped Bi_2Te_3 was studied to understand the effect of magnetic rare-earth element, Gd (GdBi) on the surface metallicity [2]. $Bi_{2-x}Gd_xTe_3$ showed a magnetic phase transition from paramagnetic to antiferromagnetic phase. Upon annealing, Gd 4d peak of x-ray photoemission spectroscopy data increased implying the out-diffusion of Gd.

In this study, we report the first-principles calculations to examine the stable Gd-related defects in Bi_2Te_3. We considered three cases for one Gd atom: adsorption on the surface, intercalation in the van der Waals (vdW) gap,and substitution for Bi (GdBi) and Te (GdTe). On the surface, there are three adsorption sites: on-top of Te, on-top of Bi (hcp), and hollow (fcc) sites.It is found that the Gd adatom at hcp site tend to kick out Bi to the surface and form a GdBi. The resulting GdBi--Bi-adatom pair (we will call this pair hcp-x.)is found to be stable configuration. In the simulated STM images, GdBi appears as a clover-shaped depression in both filled and empty state. The hcp-x is featured by a bright spot in both empty and filled state.

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First-Principles Prediction of Molecular Crystal Structures: The Role of Collective van der Waals Interactions and Vibrational Free Energies

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Molecular crystals find applications in pharmaceuticals, organic semiconductors, explosives, and in solid-state reactions. For the crystal structure prediction of molecular crystals it is imperative to calculate the lattice energies with an accuracy of about 1 kcal/mol per molecule since it is necessary to correctly rank the stability of numerous low-energy polymorphs. It has been shown that for density functional theory (DFT) the addition of van der Waals (vdW) interactions is crucial for the stability and also for the structure of molecular crystals[1]. Due to the typically large polarizabilities of aromatic molecules, having dielectric constants of about $\varepsilon = 3$, and due to qualitatively different crystal packings, vdW interactions might be highly non-local and non-additive in molecular crystals. Collective vdW correlation effects can extend to large distances, which makes them especially important for extended systems like molecular crystals. Here, we account for these effects by using the recently developed many-body dispersion (MBD) method[2]. Another challenge is that the relative polymorph stability has to be determined at room temperature in most cases. This means that instead of just DFT total energies, vibrational free energies have to be considered as well[3].
Here we study the stability and vibrational properties of several systems including low-energy structures of a “real drug” currently under investigation in the crystal structure prediction blind test of the Cambridge Crystallographic Data Centre. The accurate description of this system is quite challenging since five different polymorphic forms were determined in experiment. It is shown that inclusion of many-body dispersion interactions completely changes the relative stability of the studied polymorphs in comparison to a pairwise vdW description. Furthermore, inclusion of thermal fluctuations also leads to a renormalization of the relative stabilities. However, all experimental polymorphs are now found within an energy window of less then 3 kJ/mol per molecule. This suggests that for an accurate first-principles stability ranking of polymorphs it is necessary to go beyond state-of-the-art calculations and also include collective vdW interactions and vibrational free energies.

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General methodology for the construction of effective model potentials for lattice-dynamics simulation

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First-principles calculations using density-functional theory (DFT) are a very useful tool to study materials properties in depth. However, the big computational cost of such calculations imposes a limitation on the size of the simulated systems; thus, studying complex situations involving large simulation boxes becomes infeasible for such methods. At the expense of losing accuracy and introducing approximations, many solutions have been proposed for this problem; for example, by using coarse-graining methods, Landau-like potentials, Lennard-Jones potentials, and other approaches, the community has developed a large collection of energy functionals able to reproduce key features of the materials of interest. Recently, J. C. Wojdel and collaborators presented an atomistic approach aiming at retaining the accuracy of the DFT calculations while being computationally affordable. In order to do so, an adapted Taylor expansion explicitly compliant with the acoustic sum rule is performed in terms of atomic displacements and cell strains around a certain reference structure. The method thus constitutes a systematically improvable atomistic (electrons are not treated explicitly) approach that can in principle reproduce exactly the potential energy surface, and the main technical difficulty is to find a way to compute the model parameters in a manner that is as automatic as possible. Here we present an efficient and flexible methodology to build such models via an optimization problem. Our approach has the peculiarity of employing a suitably chosen goal function that permits an analytic solution to the fitting problem, which makes the calculations very fast and allows us to explore the parameter space in an essentially complete way. We apply the method to construct a model for feroelastic perovskite strontium titanate as a test subject. We show that our model reproduces the DFT-computed ground state properties and even high temperature energetics very accurately, and allow us to simulate the the phase transition between the antiferrodistortive I4/mcm and cubic Pm3m phases.

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A fast orbital-based ab-initio approach for Ultrafast Dynamics

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Ultrafast laser pulse experiments have recently reached femtosecond (10-15 s) time resolution, allowing access to the electronic and nuclear dynamics of many fundamental chemical and physical processes. We seek to answer a few questions: can we observe hole migration in organic molecules? Can we tune charge transfer by shaping the laser pulse? What role does nuclear motion play in these processes? While experimental work is rapidly progressing, it is very difficult to obtain information about the dynamics of the excited electrons directly. This requires us to further develop new computational methods capable of simulating coupled electron-nuclear dynamics under the influence of extremely powerful, time-dependent laser fields.

We have turned our attention to developing a fast method based on the density-functional tight-binding approach (DFTB). DFTB can be seen as an approximate DFT, which is orders of magnitude faster by using fitted matrix elements from 1-atom DFT integrals. We developed a hybrid approach, using an explicit Gaussian basis set. This allows us to approximate the hartree and exchange-correlation energy dynamically in relation to the atomic environment, which would otherwise be poorly described in a rigidly parameterized model. We additionally developed an ab-initio DFTB formalism that takes atomic polarization into account. Finally we propagate the electron-nuclear motion in the Ehrenfest approximation, which adds a basic description of non-adiabaticity to our model. The resulting method enables us to study these systems in a computationally efficient manner, which is also systematically improvable thanks to its roots in ab-initio DFT. We have applied our method to investigate charge transfer of various hydrocarbons, polymer strands, and molecular dimers and report on these.

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Reaction dynamics of CO_2 in aqueous amines from ab initio molecular dynamics

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Car-Parrinello molecular dynamics simulations, combined with metadynamics, have proven to be a useful tool for the understanding of chemical reactions. Wehave used this methodology to investigate the multi-step reactions accompanying the capture of CO_2 in aqueous amine solutions. Our results on monoethanolamine (MEA) [1], namely the chemical absorbent most frequently used for the removal of CO_2 from combustion gases, have revealed, in particular, the major role of water both on the uptake and release of CO_2 and identified as probable rate-limiting steps in the formation of the zwitterion for the former and the deprotonation of the protonated amine for the latter. As first step in the search for specific properties defining the relative performance of different amines, we have extended our study to 2-amino-2-methyl-1,3-propanediol (AMPD) [2]. We find that, although not influencing the dynamics of either the formation or the dissociation of the zwitterion, the different structure of the two molecules affects its interaction with water in a significant way, thus reducing the probability of carbamate formation and its stability in solution.

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Raman Intensities of N-layer Transition Metal Dichalcogenides from First Principles

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Transition metal dichalcogenides (TMDs) have excellent optical and electronic properties for nano-engineering applications. Raman spectroscopy is a very complete characterization tool that provides information about the vibrational modes and the optical spectrum in the same experiment: when the laser energy is close to an electronic transition, the scattered light intensity is increased due to resonance with an electronic transition.
We investigate these effects combining different computational ab-initio methods: we obtain ground-state and vibrational properties from density functional theory and the optical absorption spectrum using GW corrections and the Bethe-Salpeter equation to include excitonic effects.
Using a quasi-static finite differences approach [1], we calculate the dielectric susceptibility for different light polarizations and different phonon displacements in order to determine the Raman tensor of TMDs, in particular of multi-layer and bulk MoTe2. We seek to explain recent experimental results for the splitting of high-frequency modes [2] and deviations from the non-resonant Raman model. We also give a brief outlook on possible improvements of the methodology.
Work done in collaboration with the experimental group of IPCMS at University of Strasbourg: Guillaume Froehlicher, Ettienne Lorchat, François Fernique, Stéphane Berciaud.

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