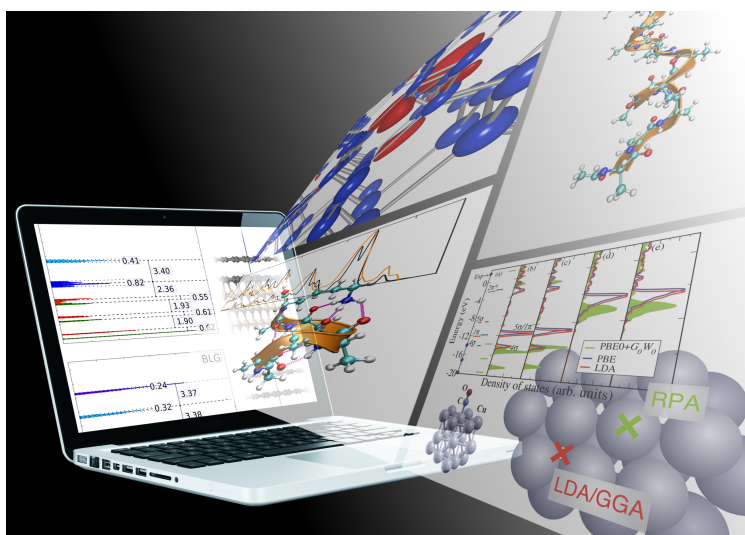




Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals

FHI-aims Developers' and Users' Meeting
August 28 - 31, 2012

Location: Free University Berlin



Organized by Fritz Haber Institute,
CECAM-scm Berlin, and CECAM-MM1P.de

Organizers

Volker Blum
Mariana Rossi
Matthias Scheffler

http://th.fhi-berlin.mpg.de/th/Meetings/FHI-aims_2012/

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1 Sponsors

FHI - Fritz Haber Institute of the Max Planck Society

CECAM - Centre Européen de Calcul Atomique et Moléculaire

CECAM - SCM Berlin node

CECAM - MM1P.de node

Ψ_k Network

Molecular Simulations from First-Principles – MS1P e.V.

NSF (MCC travel award program)

2 Practical Information

Scientific events

The morning lectures and registration will be held in the lecture hall at the Institute of Computer Science, Takustr. 9, 14195 Berlin (see map on p.7). The morning lectures are 25 minutes each plus 10 minutes for discussion.

The Hands-On Discussions and tutorials will take place in the Institute of Mathematics, rooms 0.30 and 0.31, Arnimallee 6, 14195 Berlin (see map on p.7) In these afternoon sessions, we bring participants together in small or large groups to discuss particular topics, with computers on-site if needed. The Hands-On Discussions format will allow us to develop practical answers that would not be possible within a conventional “talk/discussion” format. Topics can range from simple technical matters all the way to new physical challenges and application areas. In addition, one specific topic is singled out as a more elaborate “tutorial” on each afternoon, in parallel with the Hands-On Discussion.

The poster session takes place in the Institute of Mathematics, Arnimallee 6, 14195 Berlin on Tuesday, August 28, 2012, starting at 8pm. The posters should be put on the designated poster boards, already at the time of registration. The boards are approx. 114 cm wide and 140 cm high, meaning that a standard format such as A0 will easily fit. The label of your poster is the one indicated on the margins next to the abstract in this booklet. The posters can/should stay up throughout the workshop.

The maps on page 7 indicate the overall area of the conference (large map, below), and the details of the conference venue (smaller zoom, above). The numbers 1, 2, and 3 indicate the entrances to the Computer Science Lecture Hall, the Mathematics Institute, and the Free University Cafeteria “Mensa” (lunches) including the Galileo Restaurant (dinners on Tuesday and Thursday). As many participants are housed in the nearby Ravenna hotel, this location is also indicated on the large map (letter A).

Please do not smoke in the buildings or in the inner courtyards of the Mathematics and Computer Science institutes.

Workshop computers

We have 20 workshop computers available, which are situated in room 0.30 of the Mathematics Institute. We expect that two participants sit at each computer. If there are more participants than computers available, we ask that especially the FHI participants use their laptops instead.

Every participant has an account on the workshop computers. The information about login name and password has been distributed to each participant in the registration documents you have received.

All accounts are available on all machines, you are free to pick your favorite one, or a different one every day.

Please do not shut down, reboot or switch off any of these computers. Instead, just log off when you are done.

The computer room is available to us for the duration of the workshop, especially during the Hands-On Discussions.

Internet access

For wireless access in the Institute of Mathematics and in the Lecture Hall please use the following credentials:

SSID: conference

Key: 22m3q4qt

In order to connect you must open an arbitrary web page. Instead of the web page called, a form will appear, in which the you can enter the key provided above. Access to the wireless network will then be granted, and then you will be automatically forwarded to the web page that was originally called.

Meals

Coffee breaks take place in the lobby of the Math Building.

Lunch is provided at the FU Cafeteria “Mensa”, Otto-von-Simson-Str. 26, 14195 Berlin (see map on p.7 for details). Voucher tickets will be provided at the registration.

Dinner on Tuesday, August 28, and on Thursday, August 30, will take place in the Ristorante Galileo (on the first floor of the FU “Mensa”).

On Wednesday, August 29, the **Conference Outing** will include dinner. A separate description of the outing has been provided during the registration.

Public transport

Berlin is served by a single public transport network (BVG). Tickets are valid on all subway (U-Bahn and S-Bahn) lines as well as buses and trams. A map of the public transport network can be found on p.8. The conference site is easily reached by public transportation: Subway (U-Bahn) station **Dahlem Dorf** on the **U3 line**, within 20 minutes of the West-Berlin city center (and about 40 min of the East-Berlin city center).

Tickets can be purchased from bus drivers or from vending machines on station platforms, for instance at the subway station **Dahlem-Dorf**, near the conference location. Tickets must be stamped once for validation, either on the platform (U-Bahn, S-Bahn) or inside buses and trams. A two-hour ticket for the AB region, which covers the entire city of Berlin, costs 2,40 EUR. A short segment (“Kurzstrecke”) ticket, which is for three subway stops or six bus stops in the AB region costs 1,40 EUR. A day ticket costs 6,50 EUR. Maps of the subway and S-Bahn network are displayed on almost all station platforms.

On the homepage of the BVG (<http://www.bvg.de/index.php/en/index.html>) general information on the public transportation system in Berlin, including schedules, can be found. In particular, there are frequent connections from and to the Berlin airports and train stations, which can all be located on the network maps provided there and on p. 8.

The **bus line X83** connects the Ravenna hotel to the conference venue every few minutes during daytime, and takes about three minutes according to the schedule. The appropriate stops are “Grunewaldstr./Lepsiusstr.” (hotel) and “Arnimallee” (closest stop to conference venue). Note that you will need a “Kurzstrecke” (short segment) bus ticket for each way.

Local shops and restaurants

There are several kiosks, restaurants, a post office, and supermarket in Königin-Luise-Straße, which is the street with the bus stops of the X83 line and the U-Bahn station **Dahlem Dorf**. On weekdays, shops are typically open from 9 am to 7 pm. On Saturdays shops close at 2 pm, although some remain open until 6 pm. With very few exceptions, such as bakeries connected to a café that sell fresh rolls and cakes, all shops are closed on Sunday. However, at big train stations like Hauptbahnhof or Friedrichstraße in the city center one can find a supermarket which is open on Sundays. Banks have even more restricted opening hours and many remain closed completely on Saturdays, although cash machines can (almost) always be accessed. Of course, restaurants operate throughout the day, even on weekdays.

Going out

Concerts, parties, dancing, theater, public festivals, sightseeing walks, sport events, fairs, readings, open air - with thousands of events, the cultural variety of one of the world's most exciting cities is at your disposal. Inspiration what to do can be found on the following websites:

<http://visitberlin.de/en>

<http://www.berlin.de/international/index.en.php>

<http://www.qype.co.uk/de300-berlin>

<http://www.exberliner.com/>

<http://www.zitty.de/>

<http://www.berlin030.de/>

3 Maps

Area Map of the workshop • Free University Berlin • Berlin-Dahlem

- A** Ravenna Hotel
Grünwaldstr. 8-9
12165 Berlin
- B** Bus Stop X83
- C** U-Bahn Station
Dahlem-Dorf
- D** Fritz Haber Institute of the
Max Planck Society

- 1** **Talks**
Free University Berlin, Institute of Computer Science
Lecture Theatre (CS)
Takustraße 9, 14195 Berlin
 - 2** **Hands-On Discussions**
Free University Berlin, Mathematics Institute
Rooms 0.30, 0.31
Arnimallee 6, 14195 Berlin
 - 3** **Lunch**
FU Mensa
Otto-von-Simson-Str. 26, 14195 Berlin
- Dinner**
Ristorante Galileo, first floor
Otto-von-Simson-Str. 26, 14195 Berlin



4 Conference Program

Tuesday, August 28, 2012			
10:00 – 11:00	Mathematics Institute (FU)	Registration	
11:00 – 11:15	Lecture Hall (CS)	Introductory Remarks	
11:15 – 11:50	Lecture Hall (CS)	Volker Blum	<i>State of FHI-aims</i>
11:50 – 12:25	Lecture Hall (CS)	Sergey Levchenko	<i>Hartree-Fock and hybrid functionals, periodic: Implementation and application to defects in doped MgO</i>
12:30 – 14:00	Cafeteria “Mensa” (FU)	Lunch	
14:00 – 14:35	Lecture Hall (CS)	Jörg Meyer	<i>Phonons, FHI-aims, and the phonopy framework</i>
14:35 – 18:00	Mathematics Institute (FU)	Jörg Meyer	<i>Tutorial: FHI-aims, phonopy, and heat transport</i>
	Room 0.30	Christian Carbogno	and (in parallel)
	Room 0.31	Participants	<i>Hands-On Discussion</i>
18:30 – 20:00	Galileo Restaurant	Dinner	
20:00 – 22:00	Mathematics Institute (FU)	Poster Session	
	Foyer		
Wednesday, August 29, 2012			
09:00 – 09:35	Lecture Hall (CS)	Bruno Lang	<i>Eigenvalue solvers – The ELPA Project and Beyond</i>
09:35 – 10:10	Lecture Hall (CS)	Paula Havu	<i>Graphane on SiO₂, transport in FHI-aims</i>
10:10 – 10:45	Lecture Hall (CS)	Alexej Bagrets	<i>Electron transport through molecular junctions and FHI-aims</i>
10:45 – 11:15	Mathematics Institute (FU)	Coffee Break	
11:15 – 11:50	Lecture Hall (CS)	Xinguo Ren	<i>Beyond RPA and GW: renormalized second-order perturbation theory for ground-state and excited-state calculations</i>
11:50 – 12:25	Lecture Hall (CS)	Fabio Caruso	<i>Self-consistent GW in FHI-aims</i>
12:30 – 14:00	Cafeteria “Mensa” (FU)	Lunch	
14:00 – 16:00	Mathematics Institute (FU)	Alexej Bagrets	<i>Tutorial: The aitranss transport framework</i>
	Room 0.30		and (in parallel)
	Room 0.31	Participants	<i>Hands-On Discussion</i>
16:00 – open end		Conference Outing and Dinner	

Thursday, August 30, 2012

09:00 – 09:35	Lecture Hall (CS)	Christian Carbogno	<i>Heat transport from first principles in FHI-aims</i>
09:35 – 10:10	Lecture Hall (CS)	Mariana Rossi	<i>Ab initio molecular dynamics for biomolecular spectroscopy</i>
10:10 – 10:45	Lecture Hall (CS)	Davide Branduardi	<i>The PLUMED plug-in and free energy methods in electronic-structure-based molecular dynamics</i>
10:45 – 11:15	Mathematics Institute (FU)	Coffee Break	
11:15 – 11:50	Lecture Hall (CS)	Karsten Reuter	<i>FHI-aims becomes embedded: QM/Me and water splitting</i>
11:50 – 12:25	Lecture Hall (CS)	Scott Woodley	<i>Structure prediction and solid solutions with evolutionary algorithms</i>
12:30 – 14:00	Cafeteria “Mensa” (FU)	Lunch	
14:00 – 18:00	Mathematics Institute (FU) Room 0.30 Room 0.31	Davide Branduardi Luca Ghiringhelli Participants	<i>Tutorial: PLUMED and FHI-aims and (in parallel) Hands-On Discussion</i>
18:30 – 20:00	Galileo Restaurant	Dinner	

Friday, August 31, 2012

09:00 – 09:35	Lecture Hall (CS)	Noa Marom	<i>Keeping Supercomputers Busy – Configuration Space Exploration and GW Calculations</i>
09:35 – 10:10	Lecture Hall (CS)	Igor Ying Zhang	<i>Development of the XYG3-type doubly-hybrid functionals</i>
10:10 – 10:45	Lecture Hall (CS)	Eduardo Fabiano	<i>Non-empirical semilocal functionals for improved performance in quantum chemistry and materials science</i>
10:45 – 11:15	Mathematics Institute (FU)	Coffee Break	
11:15 – 11:50	Lecture Hall (CS)	Kenneth Jordan	<i>Exploring Intermolecular Correlation with SAPT, vdW-Corrected DFT, and Diffusion Monte Carlo Methods</i>
11:50 – 12:25	Lecture Hall (CS)	Alexandre Tkatchenko	<i>Van der Waals Interactions in Molecules, Solids, and Interfaces</i>
12:25 – 12:30	Lecture Hall (CS)	Closing remarks	
12:30	Cafeteria “Mensa” (FU)	Lunch and end of workshop	

Speaker Abstracts

State of FHI-aims

Volker Blum

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

This presentation focuses on the Fritz Haber Institute *ab initio* molecular simulations package, our implementation of “density functional theory and beyond” for molecules and materials based on numeric atom-centered orbitals. Over a period of eight years, the code has become a solid, capable framework for reliable production electronic structure theory (density functional based total energy and force methods for non-periodic molecular systems and periodic solids) and for many individual developments that build on this foundation. Recent additions cover areas as diverse as periodic hybrid functionals for solids, self-consistent *GW* and methods “beyond RPA or *GW*” for molecules, a full molecular transport framework, path integral molecular dynamics, (finally) an analytic version of the stress tensor for solids, and a host of other improvements, many of which will be discussed in depth at the workshop. In my talk, I will attempt an overview of past progress and future challenges, including some examples of large-scale applications of the code. As a whole, FHI-aims is the product of an active network of contributors both in Berlin and around the globe. This talk is dedicated to their efforts.

Hartree-Fock and hybrid functionals, periodic: Implementation and application to defects in doped MgO

Sergey Levchenko, Jürgen Wieferink, Rainer Johanni, Volker Blum, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin, Germany

Density functional theory (DFT) with standard local and semilocal exchange-correlation (XC) functionals has repeatedly demonstrated the value of finding right tradeoff between accuracy and computational cost. At the same time, numerous applications of standard DFT have clearly shown its limitations. In particular, there are practically important cases when the self-interaction error (SIE) cannot be canceled by taking appropriate energy differences. The by now well understood examples include electronic structure and bonding in ionic materials, and electron transfer. Somewhat less documented examples include effects of SIE on geometric structure.

A consistent and well-defined way to remedy SIE at least partially is to add a fraction of Hartree-Fock (HF) exchange to the Kohn-Sham equations. This hybrid DFT approach has been proven to systematically correct SIE and its consequences in some systems. However, the results of these calculations may depend on the fraction of HF exchange. While viewed by some as a conceptual failure of hybrid DFT, this dependence is interpreted by others as a tool of exploring and making the hybrid approach more flexible.

Applications of hybrid DFT to materials are still relatively limited compared to molecules, although fast-growing. The reason is the non-locality of HF exchange and the computational cost associated with it. Due to its conceptual simplicity, the hybrid Kohn-Sham scheme can be easily implemented by extending existing standard DFT codes. However, making such an implementation efficient is a non-trivial task. We here describe an implementation of periodic HF exchange (bare and screened) using numeric atom-centered basis functions within the FHI-aims [1] all-electron code. The implementation is based on a localized “resolution of identity” strategy for the Coulomb operator, combined with efficient integral and density matrix screening operations (in real space) that allow to treat periodic systems up to (currently) O(100) atoms at essentially converged basis set accuracy, and seamlessly in parallel (memory and CPU time, tested up to hundreds of CPUs). We demonstrate the performance of our approach by applying the HSE family of density functionals to defects in MgO.

[1] V. Blum *et al.*, *Comp. Phys. Comm.* 180, 2175 (2009)

Eigenvalue Solvers—The ELPA Project and Beyond

Bruno Lang

Applied Computer Science and Scientific Computing, University of Wuppertal

Eigenvalue and eigenvector computations are at the core of electronic structure simulations, and often they take a considerable amount of the overall time, in particular in highly parallel environments. One reason for this is the fact that the popular ScaLAPACK symmetric eigensolver does not scale well beyond one thousand cores, which is mainly due to the large number of memory accesses and the communication required by the two-sided transformations in the reduction phase.

We report on results from the ELPA project (*Eigenvalue Solvers for Petaflop Applications*) [1] that led to improved eigensolvers for dense symmetric problems, reducing administrative and communication overhead in existing algorithms, providing additional algorithmic paths (two-stage reduction to tridiagonal form and corresponding back transformation of the eigenvectors, divide-and-conquer algorithm and MRRR algorithm for partial eigensystems of symmetric tridiagonal matrices), and optimized computational kernels.

These routines provide significant speedup over the ScaLAPACK library, in particular if a large number of cores is used for moderately-sized matrices, and scalability has been demonstrated up to very large systems ($\sim 300k$ cores) [2].

We also briefly comment on further developments for matrices with particular structures.

[1] <http://elpa.rzg.mpg.de>

[2] R. Johanni *et al.*, Scaling of eigenvalue solver dominated simulations, in TR FZJ-JSC-IB-2011-02, pp. 27–30, April 2011

Graphane on SiO₂, transport in FHI-aims

Paula Havu, Mari Ijäs and Ari Harju

COMP / Department of Applied Physics, Aalto University, Espoo, Finland

Hydrogenation of graphene on the α -quartz (0001) SiO₂ substrate is studied, considering different surface terminations in order to take into account the amorphous nature of the substrate. Our *ab initio* calculations show that the formation of graphane by hydrogen adsorption on graphene is energetically favored on hydroxyl- and oxygen-terminated surfaces, whereas silicon termination and reconstruction of the oxygen termination hinder adsorption. Our results indicate that in order to hydrogenate graphene on SiO₂, it is beneficial to oxygenize the surface and saturate it with hydrogen.

Using the lowest energy geometries of hydrogenated graphene on the α -quartz (0001) SiO₂ substrate, we form zigzag graphene nanoribbons by selectively removing hydrogens from the epitaxial graphane layer. In these ribbons the spin degeneracy of the free-standing antiferromagnetic zigzag ribbons is broken, and band gaps of different magnitude emerge for the opposite spin channels. This degeneracy breaking is due to a charge imbalance in the substrate below the ribbon, introduced through the asymmetric alignment of the substrate atoms with respect to the edges of the graphene ribbon.

Finally a small introduction to the Landauer-Büttiker transport calculations with FHI-aims is given.

[1] M. Ijäs, P. Havu, A. Harju, and P. Pasanen, Phys. Rev. B **84**, 041403(R) (2011).

[2] P. Havu, M. Ijäs, and A. Harju, Phys. Rev. B **84**, 205423 (2011).

[3] M. Ijäs, P. Havu, and A. Harju, Phys. Rev. B **85**, 035440 (2012).

Electron transport through molecular junctions and FHI-aims

Alexei Bagrets

*Institute of Nanotechnology, Karlsruhe Institute of Technology,
76344 Eggenstein-Leopoldshafen, Germany*

In this talk, we will overview an efficient implementation of the non-equilibrium Green's functions formalism merged with non-interacting Kohn-Sham particles to evaluate electron transport characteristics of the nanoscale systems, like organic molecules establishing a contact to metallic electrodes. An efficient approximation for the self-energy will be discussed where metallic reservoirs are modeled by absorbing, energy independent, spacial boundary conditions that the Kohn-Sham wave functions are subject to [1]. A power of the approximate scheme will be demonstrated on the methodological example of the one-dimensional tight-binding wire, as well as on the example of the realistic systems like benzene-dithiol or alkane-dithiol molecular junctions with gold electrodes [2]. A comparison between computational schemes relying on the Gaussian basis functions (TURBOMOLE) and on the numerically tabulated atomic sets (FHI-aims) will be given.

Furthermore, we will discuss more elaborated schemes to construct the self-energies which allow to account for the spin-polarized electronic structure of the transition metal electrodes. We will demonstrate an ability to treat a variety of different magnetic configurations (e.g. nano-scale domain walls) which could appear when a metal-organic molecule with few spins, localized on the open shell d -ions, is brought in contact with a ferromagnetic surface and a tip of the spin-polarized-STM. Recent experiments [3,4] on the spin-polarized transport and magnetoresistance effect observed in the hydrogen-phtalocyanine STM molecular junctions will be discussed in detail.

[1] A. Arnold, F. Weigend, and F. Evers, *J. Chem. Phys.* **126**, 174101 (2007).

[2] Ch. Li, I. Pobelov, Th. Wandlowski, A. Bagrets, A. Arnold, and F. Evers, *J. Am. Chem. Soc.* **130**, 318-326 (2008).

[3] S. Schmaus, A. Bagrets, Y. Nahas, T. K. Yamada, A. Bork, M. Bowen, E. Beaurepaire, F. Evers, and W. Wulfhekel, *Nature Nanotech.* **6**, 185 (2011).

[4] A. Bagrets, S. Schmaus, A. Jaafar, T. K. Yamada, M. Alouani, W. Wulfhekel, and F. Evers, preprint (2012), under review in *Nano Lett.*

Beyond RPA and GW: renormalized second-order perturbation theory for ground-state and excited-state calculations

Xinguo Ren

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

We present a renormalized second-order perturbation theory (rPT2) [1] for the ground-state total energy that combines the random-phase approximation (RPA), second-order screened exchange (SOSEX) [2], and renormalized single excitations corrections (rSE) [3]. These three terms all involve a summation of certain types of diagrams to infinite order, and can be viewed as a renormalization of the direct, exchange, and single excitation (SE) terms of 2nd-order Rayleigh-Schrödinger perturbation theory based on an (approximate) Kohn-Sham reference state. Extensive benchmarks showed that rPT2 represents a considerable overall improvement over the standard RPA approach [1,4]. Recently we have also extended this concept to quasiparticle energy calculations. While the rSE-type correction to the irreducible self-energy does not exist, a SOSEX-type correction can be formulated rigorously using diagrammatic techniques. We show that such a correction can resolve the difficulties that the GW method encounters for the relative positions of quasiparticle excitations in certain molecules. All these developments and benchmark calculations were carried out in and with the FHI-aims code package [5,6]. Work has been done in collaboration with Patrick Rinke and Matthias Scheffler (FHI-Berlin), Joachim Paier (HU-Berlin), and Gustavo E. Scuseria (Rice Uni., Houston).

- [1] X. Ren, P. Rinke, C. Joas, M. Scheffler, *J. Mater. Sci.* **47**, 7447 (2012).
- [2] A. Grueneis, M. Marsman, J. Harl, L. Schimka, and G. Kresse, *J. Chem. Phys.* **131**, 154115 (2009).
- [3] X. Ren, A. Tkatchenko, P. Rinke, and M. Scheffler, *Phys. Rev. Lett.* **106**, 153003 (2011).
- [4] J. Paier, X. Ren, P. Rinke, G. E. Scuseria, A. Grueneis, G. Kresse, and M. Scheffler, *New J. Phys.* **14**, 043002 (2012).
- [5] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, *Comp. Phys. Comm.* **180**, 2175 (2009)
- [6] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, M. Scheffler, *New J. Phys.* **14**, 053020 (2012).

Self-consistent GW in FHI-aims

Fabio Caruso

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

In recent years, the GW approximation emerged as a predominant approach to the calculation of electronic excitations in *ab-initio* electronic structure theory. Due to its numerical cost, GW is mostly introduced perturbatively following a density-functional theory or Hartree-Fock calculation (G_0W_0). At a higher computational cost, fully self-consistent GW (sc- GW) ameliorates several shortcomings of the G_0W_0 scheme, such as the violation of particle number conservation and the dependence on the starting point [1].

We present an implementation of sc- GW – and other partially self-consistent GW approaches – in the FHI-aims code [2] based on numeric atom-centered orbitals and the resolution of the identity technique for the computation of the Coulomb integrals [3]. Finally, we present an assessment of the sc- GW approach for excited- and ground-state properties of atoms, molecules and molecular interfaces. By applying this approach to organic charge-transfer compounds – exemplified by the tetrathiofulvalene tetracyanoquinodimethane dimer (TTF-TCNQ) – we show that sc- GW provides a promising framework to predict the ground-state properties of molecular interfaces, in particular when questions pertaining to charge transfer become important.

[1] F. Caruso *et al.*, arXiv:1202.3547v1

[2] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175 (2009).

[2] X. Ren *et al.*, *New J. Phys.* **14**, 053020 (2012).

Heat transport from first principles in FHI-aims

Christian Carbogno^a, Rampi Ramprasad^b, and Matthias Scheffler^c

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^b*Institute of Materials Science, University of Connecticut, Storrs, USA*

^c*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin*

Materials with suitable thermal conductivities are crucial for a variety of applications, e.g., for the advancement of thermoelectric elements [1] or for the design of novel thermal barrier coatings for gas and airplane turbines [2]. The development and the optimization of such materials – a notoriously tedious task requiring extended and costly test series – can be considerably accelerated when aided and guided by *ab initio* calculations.

In this talk, we will cover the different *first-principles* techniques that are available to date for the assessment of thermal conductivities. We will first discuss perturbative [3] and/or non-equilibrium methods [4] that are suitable for the simulation of thermal transport at low temperatures, i.e., well below the Debye temperature. In particular, we will discuss the *laser-flash method* [5] that involves the preparation of supercells in non-equilibrium by means of the harmonic approximation. The thermal conductivity is then determined by monitoring the re-equilibration of such supercells in *ab initio MD*.

At elevated temperatures, e.g., at 70% of the melting temperature or higher, simulation techniques that rely on the harmonic approximation and/or on supercells that are unphysically far from equilibrium become questionable. These short-comings are overcome in the Green-Kubo method, which involves the assessment of the thermal conductivity from the auto-correlation of the heat flux in equilibrium *ab initio MD* [6]. We will discuss our *first-principles* formulation of the heat flux that is based on the *energy-* and *stress-densities* [7], two quantities that we have recently implemented in FHI-aims and that now allow to perform *ab initio Green-Kubo simulations*.

Eventually, we will critically discuss the computational cost, the accuracy, the convergence behavior, the limits, and the applicability of these techniques by presenting thermal conductivity data computed with the aforementioned methods for doped semiconductors and oxides.

[1] G.J. Snyder and E. S. Toberer, *Nature Materials*, **7**, 105 (2008).

[2] D. R. Clarke and C. G. Levi, *Annu. Rev. Mat. Res.* **33**, 383 (2003).

[3] D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

[4] S. Stackhouse *et al.*, *Phys. Rev. Lett.* **104**, 208501 (2010).

[5] T. M. Gibbons *et al.*, *Phys. Rev. B* **84**, 035317 (2011).

[6] R. Kubo *et al.*, *J. Phys. Soc. Jap.* **12**, 1203 (1957).

[7] R. Ramprasad, *J. Phys. Condens. Matter* **14** 5497, (2002).

Ab initio molecular dynamics for biomolecular spectroscopy

Mariana Rossi

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Accurate theoretical predictions for peptides and proteins (structure, dynamics, function) require an accurate, verified description of the underlying potential energy surface (PES). However, a completely trustworthy first-principles quality treatment that is affordable even for moderately sized systems (few hundred atoms) is arguably not yet settled. We here provide experiment-theory benchmark studies of designed polypeptides *in vacuo*, a “clean-room” environment which allows an unambiguous comparison.

We address mostly the helix-forming alanine-based Ac-Ala_n-LysH⁺ polypeptide series in the gas phase, for which experiments [1, 2] have indicated helical structures for $n \geq 8$. We explore extensively the conformational space of these molecules by performing thousands of relaxations using the van der Waals corrected [3] PBE exchange-correlation potential (PBE+vdW), as implemented in the FHI-aims program package [4]. We find that helices emerge as the preferred structure in the length range $n=4-8$ not just due to enthalpic factors (hydrogen bonds and their cooperativity, van der Waals dispersion interactions, electrostatics), but importantly also by a vibrational entropic stabilization over competing conformers at room temperature. The stabilization is shown to be due to softer low-frequency vibrational modes in helical conformers than in more compact ones, which produce significant differences in vibrational entropy [5]. This observation is in agreement with experiment [2], and with our own previous work [6], employing a quantitative comparison of calculated *ab initio* anharmonic IR spectra to experimental IR multiphoton dissociation (IRMPD) data, that show firmly α -helical structures for $n=10, 15$, and 19 at 300 K.

As an overview, benchmark energy hierarchies for Ac-Ala₅-LysH⁺ (80 atoms) using methods beyond DFT (MP2, RPA) will be shown, and limitations of the current feasible methods will be discussed. Also, recent efforts to enhance even further the quality of the PES and include quantum nuclear effects in the IR spectra of molecules through path-integral molecular dynamics and modern flexible thermostats will be briefly discussed.

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The PLUMED plugin and free energy methods in electronic-structure-based molecular dynamics

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Free energy calculations are relevant to many processes in physical chemistry. Traditionally, within the quantum chemistry community, they have been performed through static approximations that unfortunately present some limits of applicability. Only recently the increase in computing power, codes' scalability, and advances in enhanced sampling techniques are offering new chances to calculate free energies by exploiting explicit sampling of the partition function through molecular dynamics. This extends dramatically the variety of problems that one can tackle and open new avenues, especially in the soft-matter field.

In this talk I will introduce the main concepts of enhanced sampling techniques which are now incorporated into FHI-aims code by means of the open-source PLUMED[1] package.

Some simple examples of typical inputs will be provided and the variety of methods that are available will be illustrated, together with an overview on how to direct the choice towards the most suitable method for the problem under study.

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FHI-aims becomes embedded: QM/Me and water splitting

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The development of sustainable and efficient energy conversion processes at interfaces is at the center of the rapidly growing field of basic energy science. This concerns not only desired conversions, such as from solar to chemical energy, but also unavoidable by-products, such as the dissipation of chemical energy into heat. An atomistic understanding of the elementary processes involved is in all cases only just emerging but is likely to question established views and macro-scale concepts. In this context, I will review our recent endeavours to advance FHI-aims functionality towards QM/MM embedding. On the one hand, this revolves around a novel approach coined QM/Me that extends the power of embedding techniques to metallic systems. A huge atomistically described bath can thus be included in *ab initio* molecular dynamics (AIMD) simulations of chemical reactions at model catalyst surfaces. This allows to quantitatively account for the heat dissipation into the phononic system without being riddled by spurious phonon reflections as in conventional supercell AIMD simulations, while simultaneously maintaining the correct description of the metallic band structure of the extended surface. On the other hand this concerns the implementation of pseudopotential functionality to prevent charge leakage in QM/MM models for oxide semiconductor surfaces. In the talk I will sketch the versatility and numerical efficiency of this recently implemented QM/MM-approach in FHI-aims, discussing applications to charge-driven surface redox processes and in particular to direct photocatalytic water splitting.

Structure prediction and solid solutions with evolutionary algorithms

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The recent explosion of interest in the synthesis and characterisation of nano-clusters has been driven in part by the wide-ranging applications of nano-particulate materials in catalysis, electronics and energy conversion. The field has been further stimulated by the increasing need to obtain atomic level models of crystal nucleation and the early stages of growth, which also involve the formation and evolution of nano-clusters. However, elucidation of the structures and properties of nano-particulate matter is fraught with difficulties. Structure determination from experiment is often highly problematic. Diffraction may be of little if any value; small angle scattering and X-ray absorption spectroscopy can provide useful information, which, however, falls short of a detailed structural model; high resolution electron microscopy can in a number of cases provide detailed images of cluster structures, but is often difficult to apply. A range of spectroscopic techniques may be employed, but the information they give is generally incomplete and indirect. These difficulties can be related to the differing behaviour of particles of different sizes. For example, structural and optical properties of zinc oxide are crucially determined by the size of the particles. Three regimes, or length scales are recognized (cf. work on ZnO by Wood et al. [1]): Macroscopic: Particles maintain the crystal structure of the bulk; the optical band gap is practically constant, while point defects and surfaces give rise to specific size-independent phenomena, e.g. UV, blue-green, yellow-orange and red luminescence; Quantum dots: At least in one dimension, the particle size is of the order of the exciton radius, 1530\AA . (which could be still greater by one to two orders of magnitude in materials with high dielectric constant). In this regime, the bulk crystal structure is preserved even though the X-ray diffraction lines broaden, while the order of stability between the phases could change, and the optical absorption bands shift and deform, owing to quantum-size effects; Nano-Clusters: The structure of the particles may differ significantly from that of the bulk phases. Moreover, no clear diffraction patterns are obtainable, and optical properties cannot be directly correlated with those of the bulk. Indeed, for ZnO, as for other materials, there has not yet appeared an experimental technique capable of reliable characterization of the local structure; and this regime is understood least.

In my presentation I will discuss recent progress we have made [2-6] within this last size regime, namely the application of global optimisation techniques [7] as applied to predicting the atomic structure of low energy nano-clusters of inorganic compounds, the first essential step before investigating physical or electronic properties. The global search is applied to the energy landscape defined by a rigid ion and/or Shell Model (IP-landscapes), as implemented within the GULP software, as well as that defined by electronic structure techniques, as provided by the FHI-AIMS software

(the latter also being applied as a second stage for refining/re-ranking structures when searching the IP-landscapes). Our approach has recently been automated in the form of the “Knowledge Lead Master Code (KLMC)”, which manages the data and calls/reads back from external software including GULP and FHI-AIMS. Initial results from KLMC will be shown, which includes results where we have investigated the cation and vacancy ordering in bulk zinc oxide.

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Keeping Supercomputers Busy: Configuration Space Exploration and *GW* Calculations

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In this talk I will share my users perspective on running resource-intensive calculations with FHI-aims within my work on materials for organic and dye-sensitized solar cells. In order to make meaningful predictions for such systems, it is important to obtain an accurate description of the structure and electronic properties of the materials and interfaces involved. Structure prediction may require configuration space exploration, which is typically time-consuming, owing to the need to sample several hundred trial structures. The proper description of fundamental gaps and level alignment at interfaces requires memory-intensive *GW* calculations. I will discuss some examples of metal-organic dyes [1], TiO₂ clusters [2], dye-sensitized TiO₂ clusters [3], and polycyclic aromatic hydrocarbons (PAHs) [4], in terms of the required computational effort and the results obtained.

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Development of the XYG3-type doubly-hybrid functionals

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The so-called doubly-hybrid density functionals (DHDFs) incorporate the information of unoccupied orbitals in the form of second order perturbation, and stay on the fifth rung of the Jacob's ladder, according to Perdew's classification [1], close to the heaven of "chemical accuracy". Being a representative of one type of DHDFs, XYG3 shows a promising performance in predicting heats of formation, bond dissociation enthalpies, reaction barrier heights, and non-bonded interactions for chemistry of the main group elements [2,3].

However, there are several issues which call for further improvements. For example, as compared to the lower rung functionals, DHDFs are computationally more demanding, being one to two orders of magnitude higher, which prohibits their application to larger systems. Meanwhile, several recent studies revealed that XYG3 still has a tendency to underestimate the van der Waals interactions.

In this presentation, some new developments for the speedup of the DHDF calculations [4] and an improved description of van der Waals interactions will be addressed [5]. As XYG3 has now been implemented in FHI-aims, a brief introduction on this new feature will also be given in the presentation.

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Non-empirical semilocal functionals for improved performance in quantum chemistry and materials science

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The research in the field of semilocal exchange-correlation (XC) functionals is continuously asking for improved accuracy, broader applicability, and reduced empiricism. In this contribution we present our recent developments in this direction, by reporting on four *non-empirical* semilocal functionals: PBEint, zPBEint, APBE, Q2D-GGA.

The PBEint functional [1] was constructed to correctly reproduce both the slowly- and the rapidly-varying density regimes. Therefore, it performs well both for molecular and solid-state problems [2,3] and describes jellium surfaces energies without error cancellation between exchange and correlation [3]. It is especially suited to study complex problems where both density regimes coexist (e.g. hybrid interfaces, molecules on surfaces [1], metallic clusters [4]). The PBEint functional is implemented in the current version of FHI-AIMS.

The zPBEint functional [5], was designed as an extension of the PBEint functional to improve the description of spin-polarized systems, without modifying the accuracy for closed-shell cases. It significantly enhances the description of atomic and molecular open-shell systems thus improving the description of atomization and cohesive energies.

The APBE functional [6] was developed using the asymptotic expansion of the semiclassical atom. It provides very accurate results for atomic and molecular properties, and still performs well for solid-state systems. Moreover, the APBE functional is one of the most accurate semilocal approximations for the description of hydrogen bonds [2].

Finally, the Q2D-GGA functional [7] is a semilocal approximation for quasi-two-dimensional (Q2D) systems. It satisfies the nonuniform scaling in one dimension and is accurate in the whole (Q2D) regime as well as for bulk systems. The Q2D-GGA functional was shown to perform well for solid-state problems and in particular to be a valuable tool for the calculation of surface energies of many transition-metal surfaces.

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Exploring Intermolecular Correlation with SAPT, vdW-Corrected DFT, and Diffusion Monte Carlo Methods

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This talk will focus on several projects underway in the group in which weak interactions play a role. In particular, the results of symmetry-adapted perturbation theory (SAPT) for analyzing interactions in water clusters and the adsorption of water molecules on acenes will be presented. Benchmark interaction energies have also been obtained by means of quantum Monte Carlo calculations and used to assess the performance of various vdW-corrected DFT methods as well as of the RPA method.

Van der Waals Interactions in Molecules, Solids, and Interfaces

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Van der Waals (vdW) dispersion interactions are essential for determining the structure, stability, and function for a wide variety of molecules and materials [1]. In principle, ubiquitous vdW interactions can only be fully accounted for by high-level wave function methods or by Quantum Monte Carlo (QMC) techniques. In contrast, the correct long-range interaction tail, *e.g.*, for separated molecules, is absent from all popular local-density or gradient corrected exchange-correlation functionals of density-functional theory. To address this problem, we have developed an efficient method to obtain accurate vdW dispersion parameters from first principles [2], and recently extended it to determine the full long-range many-body vdW energy [3]. Our methods can be coupled to DFT calculations and even to quantum-chemical MP2 approach [4]. I will briefly discuss the theoretical underpinnings of the methods and their applications to different cases: intermolecular and intramolecular interactions [5,6], cohesion of solids [7], and the stability of organic/inorganic interfaces [8]. The performance of our approaches will be compared to both the non-local vdW-DF functional of Langreth and Lundqvist [9,10] and the exact-exchange plus correlation energy in the random-phase approximation (EX+cRPA) [11].

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Poster Abstracts

Acceleration and Direct Minimization of Electronic Structure Calculations

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The electronic ground state is determined by the electronic Schrödinger equation, but the size of the resulting problem makes it intractable for systems beyond a few electrons. Density functional theory (DFT) successfully reduces the size of the problem and permits investigation of larger problems. However, the price to pay this reduction of the model size is that DFT gives rise to a nonlinear problem which is challenging to solve. Furthermore, the calculations required at each iterative step are computationally expensive and it is therefore important to reduce the number of iterations necessary for convergence as much as possible.

We have shown that quasi-Newton (QN) method can be used to accelerate convergence towards the self-consistent field solution of the Kohn-Sham equations and increase robustness of the iteration [1]. The QN method is also suitable for use in direct minimization of the ground state energy [2]. We have also demonstrated that using an operator to update the electronic orbitals can be used to ensure that the updates remain physical [3]. Finally, this approach can be extended to ensemble DFT with fractional occupation numbers with simultaneous updates of orbitals and occupation numbers [4].

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Thermodynamic Stability of Small Mg_MO_x Clusters in Realistic Atmosphere (T, p) : Cascade Global Optimization and Atomistic Thermodynamics

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The quest for new materials demands the reliable knowledge of their (meta)stable structures under operational conditions. In particular, in heterogenous catalysis, materials operate at finite temperature, and are exposed to an atmosphere of reactive molecules in the gas phase. Thus, not only an accurate treatment of the total (electronic) energy should be aimed at, but also the degeneracy of states (related to the configurational entropy) must be taken into account to predict lowest-free-energy structures.

As a first step towards understanding the catalytic behavior of transition-metal-doped magnesium-oxide clusters, we study the stability of magnesium clusters in an atmosphere of oxygen. We employ a massive-parallel cascade genetic algorithm (cGA), together with *ab initio* atomistic thermodynamics (*aiAT*). The underlying concept of cGA is to perform an exhaustive genetic-algorithm pre-scanning of possible structures at various stoichiometries by means of a computationally inexpensive reactive force field. The low energy structures found with this scanning are used as initial guess for a less extensive genetic-algorithm scanning with fitness function based on density functional theory. Structures are locally minimized at the van-der-Waals corrected PBE level, but the energetics are calculated at higher level, e.g. HSE06, PBE0, RPA@PBE0. The cGA output structures are then examined by applying the concept of *aiAT* to analyze the (T, p) dependence of the composition, structure, and stability of the various isomers for each size M of these Mg_MO_x clusters in oxygen atmosphere.

Our results show that at realistic pressures and temperatures, non-stoichiometric clusters with $x > M$ are more stable when $M = 1-5$, while for bigger clusters (e.g., $M = 10$), the stoichiometric composition $((MgO)_n)$, albeit with non-bulk-like geometries, is strongly preferred.

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

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Nanostructured oxide surfaces promise a wide range of applications in surface chemistry and catalysis. Exploring the zoo of combinatorial compound material for the ultimate candidate for a certain application may best be tackled by computational studies. When addressing those functionalities through quantitative first-principles calculations, applying periodic boundary conditions (PBC) becomes numerically inefficient or even unfeasible at a certain system size, especially when going beyond the semi-local DFT level of theory. Exploiting the localized character of those systems we develop a highly efficient embedding setup to overcome limitations through system size. In this setup the nanostructure and immediate oxide surrounding is described quantum mechanically, while the long-range electrostatic interactions with the support are accounted for through a monopole field. A transition shell between both regions is introduced to prevent electron leakage into the Coulomb singularities and wrong chemical behavior through the creation of dangling bonds at the boundary of the quantum mechanical (QM) zone. In this transition shell oxide particles are represented through norm-conserving pseudopotentials [1] in the fully separable Kleinman-Bylander form [2]. We report details of the implementation of this scheme into the FHI-aims package [3]. For the optimization of the model parameters (size of QM-region, thickness of connecting shell) we reference against supercell geometry data, exploiting the FHI-aims capability to treat finite cluster and PBC supercells within the same numerical framework. With optimized parameters we achieve a speed-up in computation time in the order of 10 compared to PBC calculations. Not being restricted to PBC calculations, the developed set-up is ultimately also capable to efficiently deal with charged states, which will be a fundamental asset for the description of charge transfer processes e.g. in photoinduced catalysis.

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Investigation of structure and reactivity of bimetallic surface alloys using FHI-aims

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Since bimetallic surface structures often exhibit catalytic activities and selectivities higher than their pure components, there is a strong interest in understanding the factors leading to this particular behavior. In this contribution we address the study of PdAg/Pd(111) surface alloys based on density functional theory (DFT) calculations using a numbered atomic orbital (NAO) basis set, as implemented in the FHI-aims code. We also compare the results obtained using the NAO basis set with those obtained using a plane-wave basis set in order to have a reference. Interpretation of the results is based on the outcome of a recent experimental study of the structural and catalytic properties of PdAg/Pd(111) upon CO exposure carried out using a combination of various UHV techniques.[1] Since the catalytic activity is a result of the interplay between different effects, such as electronic ligand and geometrical effects, we analyze different geometric configurations of the surface alloy in order to reveal how such effects can contribute to the reactivity, and to understand the behavior of the system under effect of CO exposure.[2]

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KLMC: A parallel computer program for structure prediction on the DFT energy landscape

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We introduce a recently developed parallel computer program for structure prediction; KLMC (Knowledge-Led Master Controller). The KLMC is a computer program that uses the MPI parallelism strategy, and is capable of searching the energy landscape using empirical potentials, Density-Functional Theory (DFT) or both, using a Genetic Algorithm. Appropriate for this workshop, we use the popular code; FHI-aims [1] (compiled as a library) to perform geometry optimizations of the candidate structures. We demonstrate the KLMC on a range of nano-clusters; $(\text{MgO})_n$ and $(\text{ZnO})_n$, where $n = 1 - 15$, and show that it efficiently finds the ground-state structures.

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Towards *ab-initio* transport calculations for molecular materials.

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In recent years, experimental progress has advanced so that electron transport properties of molecular structures become accessible in laboratories in a routine fashion. In the current focus are molecular systems like single organic molecules, graphene ribbons or functionalized graphene flakes, carbon nanotubes and many other structures.

In order to gain a better understanding of the detailed transport characteristics and of how they relate to the molecular structure of the system, *ab-initio* calculations are indispensable. Such *ab-initio* transport studies already exist for the field of Molecular Electronics, but they are not yet available for the broader scope of molecular materials in general.

In our project we build up a machinery for transport calculations suitable for the investigation of transmission properties of meso-sized molecular systems. To this end, we are extending the AITRANSS-module already available in FHI-aims [1-3]. We aim at parallelizing the transport code so that larger systems become computational feasible.

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Towards understanding the role of dispersion interaction in molecular crystals

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Molecular crystals are among some of the most interesting and challenging condensed-matter systems to study, with a wide range of applications in areas such as pharmaceuticals, solar cells and food science. Standard local and semi-local density functionals perform poorly for these systems due to a lack of dispersion interactions, which can be pivotal for the structure and properties of molecular systems. In recent years many schemes for correcting density functionals have been developed, with the most successful adding a pairwise correction (based on C_6/R^6) to the DFT energy [1,2].

While such schemes can dramatically improve the DFT picture of molecular crystals, they ignore a number of important contributions. In this work we outline a recently developed approach to including screening and many-body dipole contributions [3] and apply it to a number of important model molecular crystals, including nitromethane, naphthalene and aspirin. The method builds on the Tkatchenko-Scheffler scheme [2] and treats each of the atoms as a dipole oscillator. Coupling the oscillators using classical electrodynamics first yields screened polarisabilities, C_6 and R_0 values, with a second step considering all of the dipole-dipole many-body interactions in a coupled fluctuating-dipole model [4]. In some instances the arrangement of atoms and molecules leads to significant increases and decreases in dispersion interactions, while in others little change is seen, potentially explaining the hit-and-miss nature of the pairwise methods. The results demonstrate the anisotropic and non-additive nature of dispersion interactions in molecular crystals and offer new insights into the use of such interactions in crystal engineering.

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Quantum nature of the hydrogen bond

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Hydrogen bonds are weak, generally intermolecular bonds, which hold much of soft matter together as well as the condensed phases of water, network liquids, and many ferroelectric crystals. The small mass of hydrogen means that they are inherently quantum mechanical in nature, and effects such as zero-point motion and tunneling must be considered, though all too often these effects are not considered. As a prominent example, a clear picture for the impact of quantum nuclear effects on the strength of hydrogen bonds and consequently the structure of hydrogen bonded systems is still absent. Here, we report *ab initio* path integral molecular dynamics studies on the quantum nature of the hydrogen bond. Through a systematic examination of a wide range of hydrogen bonded systems we show that quantum nuclear effects weaken weak hydrogen bonds but strengthen relatively strong ones. This simple correlation arises from a competition between anharmonic intermolecular bond bending and intramolecular bond stretching. A simple rule of thumb is provided that enables predictions to be made for hydrogen bonded materials in general with merely classical knowledge (such as hydrogen bond strength or hydrogen bond length). Our work rationalizes the influence of quantum nuclear effects, which can result in either weakening or strengthening of the hydrogen bonds, and the corresponding structures, across a broad range of hydrogen bonded materials. Furthermore, it highlights the need to allow flexible molecules when anharmonic potentials are used in force field-based studies of quantum nuclear effects. For more detail of this work, please see Ref. [1].

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Band Structure and Optical Properties of Doped Hematite

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We present [1] a hybrid density functional theory (DFT) study of doping effects in α -Fe₂O₃, hematite. Standard DFT underestimates the band gap by roughly 75% and incorrectly identifies hematite as a Mott-Hubbard insulator. Hybrid DFT accurately predicts the proper structural, magnetic, and electronic properties of hematite and, unlike the DFT+U method, does not contain *d*-electron specific empirical parameters. We show the antiferromagnetic symmetry in the pure α -Fe₂O₃ crystal is broken by all dopants and that ligand field theory correctly predicts local magnetic moments on the dopants. We characterize the resulting band gaps for hematite doped by transition metals. The specific case of Pd doping is investigated in order to correlate calculated doping energies and optical properties with experimentally observed photocatalytic behavior.

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**Two related peptides exhibiting extremely different folding characteristics:
Ac-Ala₁₉-Lys + H⁺ vs. Ac-Lys-Ala₁₉ + H⁺**

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Predicting the structure of peptides requires a method with high accuracy for “weak” interactions. We here employ density-functional theory with the PBE functional corrected for van der Waals interactions [1] as implemented in the FHI-aims code [2] to demonstrate the extreme change of folding characteristics due to only a trivial shift of one amino acid in the sequence: Ac-Ala₁₉-Lys + H⁺ versus Ac-Lys-Ala₁₉ + H⁺. We here show that Ac-Ala₁₉-Lys + H⁺, a known helix former [3,4], is a clear structure-seeker exhibiting only one smooth folding funnel, while Ac-Lys-Ala₁₉ + H⁺ shows the characteristics of a glass-former [5], i.e. multiple folding funnels that are similar in energy. Ac-Lys-Ala₁₉ + H⁺ presents an experimental puzzle that we solve by theoretical means: While earlier ion mobility measurements suggest the formation of compact globular structures [3], experimental IR spectra in the present work [6] are similar to those of helices. We apply a two-step structure search method, starting with force-field based replica exchange molecular dynamics (REMD) and following up with first-principles REMD. The predicted low-energy structures are all compact, but with significant helical content. Calculated IR spectra of the lowest-energy conformers show that this helical content does explain the overall similarity to an actual helix spectrum.

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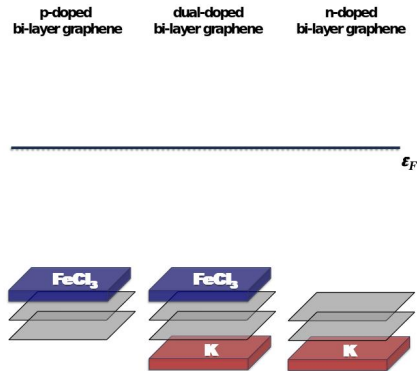
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Gap Controls of Bilayer Graphene by Dual Doping Method

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The band gap opening of graphene is the most desired property in device industry because it is vital to the application of graphene as a logical device of semiconductors. Here, we show how to make a reasonably wide band gap in graphene. This is accomplished with bilayer graphene (BLG) dual-doped with FeCl₃ acceptor and K donor. To elucidate this phenomenon, we employed the first principles method taking into account van der Waals interaction. For the FeCl₃ adsorbed BLG, the optimal distance between the adjacent graphene and FeCl₃ layers is 4.6~4.8 Å, consistent with experiments. Due to high electronegativity of FeCl₃, these graphene layers are hole-doped. The dual-doped BLG gives band gap of 0.27eV due to broken symmetry, with Dirac point shift by -0.09 eV. This increased band gap and proper Dirac point shift could make the dual-doped BLG useful for applications towards future field effect transistor devices. [1, 2]

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FHI-aims based embedded cluster modeling of catalytic processes in zeolites: N₂O adsorption on Fe-silicalite

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Our embedded cluster hybrid QM/MM model for zeolitic materials is realised in the computational chemistry environment ChemShell [1,2]. In this work, the software is extended to interface with the FHI-aims code [3], implemented as a QM driver, and tested against our previous calculations employing Gaussian basis sets as implemented in Gamess-UK [4]. The FHI-aims interface has been developed in collaboration with Johannes Kästner and Volker Blum, FHI Berlin.

In particular, we consider the structure and properties of a conventional Brønsted acid site, substitutional and an inverted Ti and Fe(II) active sites, the structures of which have been postulated in our previous studies [5,6]. Furthermore, we investigate the adsorption of N₂O on the Fe site, which results in Fe oxidation. This process is generally accepted as the first step in the partial oxidation of alkenes over Fe-silicalite systems, and presents a considerable theoretical challenge due the complex electronic processes involved.

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1D atom and molecule wires on silicon surface

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The development of modern nanoelectronics relies crucially on the identification of various novel types of quantized structures. In particular, the artificially synthesized quantum one-dimensional (1D) structures show a variety of intriguing physical phenomena distinct from their bulk counterparts due to the confinement of electrons in only one direction. In most of the 1D structures, the significantly enhanced couplings between charge, lattice, and spin degrees of freedom could lead to exotic phenomena such as Peierls instability, spin orderings, and the formation of Luttinger-liquid ground state. Using first-principles density-functional calculations, we investigate the competition between Peierls instability and spin orderings in the dangling-bond (DB) wires fabricated on silicon surfaces [1] and graphene [2]. We found various quantum-size effects in the energetic, geometries, and electronic states of the DB wires as a function of their length. Besides the presence of exotic ground states, potentially even more intriguing are their elementary excitations. We present a combined STM and first-principles study for the structural and electronic properties of quasi-1D indium chains on Si(111) surface, including the structure, energetics, and dynamics of topological solitary excitations or solitons at the atomic scale [3]. Based on first-principles density-functional calculations, we propose novel growth mechanisms of the 1D molecular lines on the H-terminated Si(001) surface. We present a facile method for the self-directed growth of 1D molecular lines along the Si dimer rows [4]. Instead of a previously employed single dangling bond, we here employ a single H-free Si dimer as a reaction site, resulting in an enhanced stability of the radical intermediate for the Ophthalaldehyde (OP) molecule containing two carbonyl groups. This radical intermediate easily abstracts two H atoms from a neighboring Si dimer, thereby allowing the chain reaction for a 1D molecular line. Such a fabricated OP line will be stable at higher temperatures compared to previously reported alkene lines because of its enhanced stability. We also propose a growth mechanism of the recently observed allyl mercaptan line, where the line is directed across the Si dimer rows [5]. The proposed structural model shows that the molecules adsorb across two Si dimers in the adjacent dimer rows with the Si-C and Si-S bonds, thereby yielding a higher thermodynamic stability compared to other alkene lines (containing a single Si-C bond per molecule) grown along the dimer rows.

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Dielectric Properties of Carbon, Silicon and Germanium Based Polymers: A First Principles Study

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A knowledge of factors that control the electronic structure and dielectric constant of materials would be valuable in the design of new insulators with attractive dielectric properties. In an attempt to systematically and directly understand the role of chemical composition and atomic configuration in determining such properties, we have studied (using first principles computations) nine homopolymer systems based on XY_2 building blocks, where $X = C, Si$ or Ge and $Y = H, F$ or Cl . Two possible generic configurations were explored, and our computations utilized dispersion-corrected semilocal exchange-correlation functionals as well as hybrid functionals. Correlations between stability, electronic structure features, infrared intensities and the dielectric response are established across the chemical and configurational space considered. Homopolymers containing GeF_2 or $GeCl_2$ building blocks are identified as particularly promising. These systems display large dielectric constant values (regardless of the underlying crystal structure), and may display a large band gap for particular configurations. The design of a polymer insulator with optimal dielectric constant and band gap may require consideration of heteropolymers (e.g., involving CH_2 and GeF_2 building blocks). We provide a strategy for the rapid and accurate exploration of that extended chemical and configurational space.

Modeling of (de)intercalation in Li-ion battery materials: Structural stability of FePO_4 from *ab initio* calculations

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The increasing demand for mobile energy storage requires improved Li-ion batteries, in particular with respect to cycle life, power density and charging time. However, even for commercially widely established cathode materials in Li-ion batteries, the details of the (de) intercalation kinetics are not yet fully understood. We aim to contribute to a better understanding by modeling the intercalation for FePO_4 cathode materials. To this end, we determined the structural stability of Li-Fe-P-O systems using high-throughput density-functional theory calculations. We use the projector augmented wave (PAW) method and GGA and GGA+U exchange-correlation functional. We determined the heats of formation at $T=0$ for Li_xFePO_4 for the full range of de-intercalated ($x=0$) to intercalated ($x=1$) structures. For the fully intercalated structures, the calculated lattice constants are in very good agreement with experiment while for the deintercalated structures we find a few percent deviation to experiment. The calculated heats of formation of Li_xFePO_4 compare well with experimental measurements and previous calculations. This work is part of a collaboration within the SPP1473 WeNDeLIB priority program.

Catalytic activity of core-shell nanocluster based on platinum for oxygen reduction reaction: all-electron DFT study

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In a fuel cell device such as proton exchange membrane (PEMFC), the catalytic activities on each electrode play a pivotal role in determining a whole performance. Platinum has been widely used since it exhibits excellent catalytic activity in this device, however, there is a serious hindrance due to high cost and small reserves for commercialization. It is needed to discover a novel catalyst that has lower cost and stronger activity than that of platinum catalyst. Recently, many researches have been done for the binary alloys composed of core-shell structure based on platinum by using various transition metals. In this way, theoretical screening method such as density functional calculations has been regarded as a power tool for searching a novel catalyst. We have studied the catalytic activity of Pt-based alloy for the oxygen reduction reaction (ORR) on anode in PEMFC. Since the full mechanistic study on the catalytic activity of Pt-based alloys requires much computational cost, we simplified the problem to find a key descriptor, adsorption energy. According to the Sabatier relation, the adsorption energy is directly related to the catalytic activity and the activity shows so called volcano curve. Finding an alloy shows the optimal adsorption energy is equivalent to find an alloy having optimal catalytic activity. As an alloying element, we considered Ni, Cu, Ru, Rh, Pd, Ag, Ir, Au and Pb and assumed these elements acted as a core material. We compared the adsorption energy between these core-shell nanoclusters and the pure Pt nanoparticle and investigated a chemical trend among these metals. The details will be presented in later.

Computational study of Hybrid GaAs/Polymer Solar Cells

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We report the study of hybrid solar cells consisting of GaAs as the n-type and a polymer as the p-type semiconductor. In our system of interest, GaAs is made into nanopillars with a top orientation of (111) and six (110) side walls. There are major advantages to the use of nanopillars including a dramatic reduction to the leakage current. Our project goal is to improve the efficiency of the hybrid solar cell system by making changes such as the type of polymer semiconductor used. To that effect, we model the interface between the GaAs and the polymer to better understand the properties.

We use FHI-aims to model the binding energy of passivating agents (octanethiol, sulfur) on the (110) GaAs surface. This result will help us determine the surface binding sites and optimum coverage. With the determined surface, we study how the polymer semiconductor will interact with the surface using a combination of force field and DFT methods. We use AIMS to measure the band gap, and to demonstrate the abilities of the code's hybrid functionals to predict surface or bulk band gaps. The measurement of band gaps will help us predict the best combination of polymers and passivating agents, and will lead us to a better understanding of the electron transfer mechanism.

Excess electron binding to water clusters and fullerenes in non-valence states

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The accurate description of quasiparticles in molecules requires a proper balance of exchange and correlation interactions. Two of the most popular methods for calculating ionization potentials and electron affinities used by the quantum chemistry community are the equations of motion (EOM)[1] and algebraic diagrammatic correction (ADC)[2] methods. In the context of Hedin's equations[3] these can be viewed as providing a self-consistent description of G , with W_0 , along with vertex corrections. In other words, they can be termed $GW_0\Gamma$, with various approximations for W_0 (not necessarily the infinite-order rings (RPA)). On the other hand, in the physics community, the quasiparticle energies are calculated using the GW methods.

In this work, we discuss the various aspects of excess electron binding energies to water clusters and fullerenes, in non-valence states, using the above methods and highlight the similarities and differences of various methods diagrammatically. Benchmark accurate electron binding energies for water clusters[4] are used to develop one electron model potentials and are shown to give good performance.[5] We also discuss the model potential for electron binding energies to fullerenes which is under development.

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First-Principles Thermodynamic Stability of Acids and Bases under pH Environment: a Microscopic pH Theory

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Despite being one of the most important thermodynamic variables, pH has yet to be incorporated into first-principles thermodynamics to calculate stability of acidic and basic solutes in aqueous solutions. By treating the solutes as defects in homogeneous liquids, we formulate a first-principles approach [1] to calculate their formation energies under proton chemical potential, or pH, based on explicit molecular dynamics. The method draws analogy to first-principle calculations of defect formation energies under electron chemical potential, or Fermi energy, in semiconductors. From this, we propose a simple pictorial representation of the general theory of acid-base chemistry. By performing first-principles molecular dynamics of liquid water models with solutes, we apply the formulation to calculate formation energies of various neutral and charged solutes such as H^+ , OH^- , NH_3 , NH_4^+ , HCOOH , and HCOO^- in water. The deduced auto-dissociation constant of water and the difference in the pKa values of NH_3 and HCOOH show good agreement with known experimental values. Our first-principles approach can be further extended and applied to other bio- and electro-chemical molecules such as amino acids and redox reaction couples that could exist in aqueous environments to understand their thermodynamic stability.

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Mechanochemistry of small molecules: into which bond does the force go?

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Regulation of (Bio)chemical reactions by mechanical force has been proposed to be fundamental to cellular functions[1]. Atomic force microscopy and molecular force probe experiments suggested an enhancement on the reactivity of thiol/disulfide exchange[2] and ring-opening of cyclobutene[3], respectively. Recently, we have performed hybrid quantum mechanical molecular mechanical simulations in combination with transition path sampling on the thiol/disulfide exchange. We could show that stretching a molecule can significantly shift the transition state, and also affects degrees of freedoms other than sole bond stretching [4].

In order to understand into which degrees of freedom the force goes, we have developed a force distribution analysis method for ab initio simulations, a simple scheme to deduce pairwise forces from non-pairwise quantum mechanical descriptions, which is transferable to any other (bio)chemical molecule for which internal stresses are of interest. The application to the ring-opening of cyclobutene shows how mechanical stretching forces propagate into the bonds of the reactive system, leading to both compressive and tensile forces in the strained cyclobutene. The force distribution allows to directly relate internal forces in bonds to mechanochemical events of bond scission.

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Ultra-thin ZnO films on metal substrates from first principles

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In the context of hybrid inorganic/organic interfaces, ZnO is developing into a popular inorganic component. To prevent charging or conductivity problems in surface sensitive characterization techniques such as scanning tunneling microscopy or photoemission spectroscopy, metal supported ultra-thin ZnO films can be used as model systems. By means of density-functional theory (DFT) calculations we investigate to what extent ultra-thin ZnO on the (111) surfaces of Ag, Cu and Pd resembles the properties of bulk ZnO surfaces or if it should be regarded as a distinct nanosystem in its own right [1]. Free standing ZnO mono-layer thin films deviate from the wurtzite structure of the bulk material and adopt a planar, graphite-like geometry, in agreement with previous calculations [2]. By inspecting the stress/strain curve of the freestanding mono-layer the expected commensurability condition for different substrates can be estimated. The DFT calculations reveal that the ZnO/metal interaction is weak. The results will be analyzed in terms of the underlying electronic structure, the effect of the exchange-correlation functional and the thickness of the ZnO layers.

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Theoretical Record Spin Filtering in Graphene based Spin Valves

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Using first principle computational methods [2,3] and different approaches to electronic transport [4,5], we study spin polarized transport through graphene based spin valves. Concluding that it is theoretically possible to achieve virtually perfect spin filtering by using a Ni|Graphite|Ni geometry. This selectivity is based on graphene[1] and graphite's peculiar Fermi Surfaces and the selective overlap of them with the Ni Fermi Surface for one spin direction only (minority). Furthermore, we report record values of MR in these junctions. Our findings could be extended to other ferromagnetic metals of similar symmetry as Ni. If confirmed experimentally, our results will be of high technological value for the continuing progress of MRAMs.

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