Report on Workshop Density-Functional Theory and Beyond with Numeric Atom-Centered Orbitals

Harnack House of the MPG in Berlin, Germany

August 19 to 22, 2014

sponsored by Psi-k

Christian Carbogno, Carsten Baldauf, Volker Blum, Matthias Scheffler

http://th.fhi-berlin.mpg.de/sitesub/meetings/FHI-aims-2014/

The "FHI-aims Developers' and Users' Meeting" was held at the Harnack House in Berlin from August 19 to 22, 2014. About 50 scientists attended the meeting to discuss recent progress in localized basis set methods for electronic structure theory. The talks covered quite diverse areas of research that can be roughly grouped into four categories:

1. *Accuracy of numerical algorithms and methods:* In spite of their success, the limitations of density-functional theory (DFT) at the local (LDA) and semi-local (GGA) level of theory are, in some areas, severe. Part of the talks focused on how these limitations can be overcome by the development of higher level techniques (e.g. self-consistent GW as well as periodic G_0W_0 and RPA) and on how these methods can be applied to extended systems via embedding.

2. *Push towards large system sizes:* Over the last decades, the focus of electronic structure theory has shifted towards more realistic simulations that require assessing large system sizes (>1000 atoms), huge chemical and conformational phase spaces, and/or long timespans (>1ns). This research field was covered by various talks that for instance discussed genetic algorithms for structure search, extrapolation techniques to achieve time- and size-convergence in thermal conductivity simulations, and transition state search for long time scale dynamics.

3. *Novel and efficient post-processing:* Extracting more advanced and complex data (such as higher-order derivatives) from DFT calculations

and linking this data to algorithms from statistical mechanics is a key step to model realistic thermodynamic conditions. This field was well represented in the meeting with, for instance, talks on density functional perturbation theory and path-integral molecular dynamics. Along these lines, the systematic statistical analysis of the vast and complex data generated in such approaches was discussed as well (Big data of material science).

4. *Computational efficiency and change of computational resources:* Sustained numerical efficiency across computer architectures and code paths is the key factor that enables the advanced computations discussed in (1)-(3). The talks in the meeting presented the computational framework (localized resolution of identity) at the heart of "beyond LDA/GGA" techniques and discussed advanced (mixing and preconditioning) algorithms. Furthermore, the programming paradigms required on novel computational architectures were the topic of one talk as well.

Beside the scientific talks, the program featured a poster session and "Hands-on Discussions and Tutorials" with computers on site. The tutorials were mainly intended to introduce the audience to newly developed features in the FHI-aims code package (embedding, genetic algorithms) and to external software frameworks (i-PI for path integral MD, the Virtual Nanolab GUI and scripting language) that were recently linked to FHI-aims. In parallel, "Hands-on Discussions" in small groups allowed an efficient communication between developers, users, and newcomers on specific topics that ranged from "using the distributed versioning system GIT effectively" over "achieving self-consistency" to "wish list in code and feature development". As organizers, we could not be more delighted with the meeting: It was a pleasure to see the lively discussions that encompassed young Ph.D. students and established researchers alike. As a matter of fact, the scientific conversations and debates were not limited to the afternoon sessions, but leaked into dinner and even spontaneously lead to an evening session on the "best practices of scientific software development".

Programme

The workshop featured 20 talks, 5 tutorials, and various HandsOn discussion session.

Tuesday, August 19		
10:40 - 11:15	V. Blum	State of FHI-aims
11:15 - 11:50	T. Schulthess	Towards extreme-scale electronic simulations for materials design: algorithms and methods for novel computing architectures
11:50 - 12:25	D. Berger	Embedded-Cluster Calculations in a Numeric Atomic Orbital Density-Functional Theory Framework
14:00 - 15:30	K. Stokbro	Hands on session: FHI-aims in the Virtual NanoLab
15:30 - 17:00	Track 1	Embedding walk-through (D. Berger)
15:30 - 18:00	Track 2	Hands-on Discussions
17:00 - 18:00	Track 1	GIT Tutorial (A. Ihrig)
18:00 - 19:00	Poster parade	2 min. talks by all poster authors
Wednesday, August 20		
9:00 - 9:35	A. Bagrets	Electron Transport at the Molecular Scale within FHI-aims
9:35 - 10:10	B. Bieniek	HDF5 and ESP-Charges in FHI-aims
10:10 - 10:45	V. Havu	Finding the Ground State: Mixing and Preconditioning
11:15 - 11:50	T. Körzdörfer	G_0W_0 Calculations based on Non-empirically Tuned Long-range Corrected Hybrid Functionals
11:50 - 12:25	M. Rossi	Path Integral Molecular Dynamics for Nuclear Static and Dynamical Properties: The i-PI-FHI-aims Interface
14:00 - 16:00	Track 1	PI-MD Tutorial (M. Rossi)
14:00 - 15:00	Track 2	Hands-on Discussions on Hybrid functionals
15:00 - 16:00	Track 2	Hands-on Discussions on exchange and correlation beyond DFT

Thursday, August 21

9:00 - 9:35	A. Tkatchenko	From Dispersion Interactions to Farsighted Electron Correlation – A Unified Approach Based on Atomic Response Functions
9:35 - 10:10	G. Henkelmann	Using Density Functional Theory to Model Transition States and Long Time Scale Dynamics
10:10 - 10:45	C. Carbogno	Thermal Conductivity Simulations: Achieving Time and Size Convergence
11:15 - 11:50	H. Shang	Density-functional Perturbation Theory for Lattice Dynamics in FHI-aims
11:50 - 12:25	C. Baldauf	Structure and Dynamics of Peptide Foldamers from First Principles
14:00 - 14:35	S. Bhattacharya	Property based Cascade Genetic Algorithm Implementation for Efficient Scanning of $(TiO_2)_n$ clusters: Structure Matters more than Size
14:35 - 17:00	Track 1	GA Tutorial (A. Supady and S. Bhattacharya)
14:35 - 16:00	Track 2	Hands-on Discussions on efficiency and scaling
16:00 - 17:00	Track 2	Hands-on Discussions on SCF stability
20:00 - 21:00	Track 2	Hands-on Discussions on wrappers, new directions, and implicit solvent

Friday, August 22

9:00 - 9:35	A. Ihrig	Localized Resolution of Identity: Accurate and Efficient Evaluation of the Coulomb Operator for Advanced Electronic Structure Methods
9:35 - 10:10	X. Ren	Implementation of Periodic RPA and GW with Numerical Atomic Orbitals
10:10 - 10:45	I.Y. Zhang	Assessment of Density Functionals in FHI-aims: Searching for the Next-generation Density Functional with a Broader Application
11:15 - 11:50	F. Caruso	Self-consistent Many-body Approaches in FHI-aims
11:50 - 12:25	M. Scheffler	Big Data of Materials Science from First Principles – Critical Next Steps
12:25 - 12:35	The organizers	Closing remarks

Report on Workshop Density-Functional Theory and Beyond with Numeric Atom-Centered Orbitals

Harnack House of the MPG in Berlin, Germany

August 19 to 22, 2014

sponsored by Psi-k

Christian Carbogno, Carsten Baldauf, Volker Blum,
Matthias Scheffler

http://th.fhi-berlin.mpg.de/sitesub/meetings/FHI-aims-2014/

Speaker Abstracts

S 1

State of FHI-aims

Volker Blum
Duke University,
Department of Mechanical Engineering and Materials Science, Durham,
NC 27708, USA

FHI-aims has just seen its tenth anniversary and is going strong as an efficient, accurate all-electron platform for first-principles computational molecular and materials science. This talk highlights some recent accomplishments and future directions for FHI-aims.

S 3

Embedded-Cluster Calculations in a Numeric Atomic Orbital Density-Functional Theory Framework

Daniel Berger[1], Andrew J. Logsdail[2], Volker Blum[3], and Karsten Reuter[1]
1: TU München, Lichtenbergstraße 4, 85747 Garching
2: University College London, Department of Chemistry, 20 Gordon St.,
London, UK
3: Duke University, MEMS Department, Durham, NC 27708, USA

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. 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. We illustrate the performance of various levels of theories using the water-splitting reaction at ideal and defected TiO2 (110) surfaces as showcase.

[1] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67-98, (1999)
[2] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425-1428, (1982)

S 4

Hands-on Session: FHI-aims in the Virtual NanoLab

Kurt Stokbro
QuantumWise A/S
Lersø Parkalle 107, DK-2100 Copenhagen, Denmark

The FHI-aims code is now integrated into the Virtual NanoLab (VNL) from QuantumWise[1]. VNL is a graphical user interface which allows for building advanced geometries, setting up quantum simulations and analyzing output data. It interacts with a number of different atomic-scale simulators through a common python interface. In this talk I will give an overview of the integration of FHI-aims and the new capabilities available through VNL. There will be a hands on session where it is possible to try out the new interface[1], and an overview of the implemented and coming features will be presented. Feature requests will also be welcome.

[1] The VNL is part of the Atomistix ToolKit 2014 and can be downloaded from:

http://www.quantumwise.com/download

It comes with an installer and includes a 14 days trial license. It is recommended that the participants download and install the software before the session.

S 5

Electron Transport at the Molecular Scale within FHI-aims

Alexej Bagrets
Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT),
76344 Eggenstein-Leopoldshafen, Germany

We will overview a preliminary implementation of the self-consistent non-equilibrium Green's function formalism for electron transport within the FHI-aims code. This implementation will be confronted with that one based on the Gaussian orbitals within the TURBOMOLE quantum chemistry package. Applications to experimentally relevant systems will be discussed, including a magnetoresistance effect through organic molecule, STM experiments on the metal-organic complexes showing Kondo effect, as well as bias-voltage induced forces in single molecule junctions.

S 6

HDF5 and ESP-Charges in FHI-aims

Björn Bieniek and Patrick Rinke
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

Using hybrid inorganic/organic systems (HIOS) as an example, I will present the implementation of the HDF5-container-file library [1] and electro-static potential charges (ESP) in FHI-aims. We approached HIOS by combining first-principles electronic structure theory (e.g. density-functional theory (DFT)) with a density-matrix based formalism to model the charge carrier dynamics of photoexcited molecules on the ZnO 10-10 surface [2]. We obtain optical transition matrix elements for the ladder-type quarterphenyl molecule (L4P) and the ZnO surface from DFT calculations. These matrix elements are written to HDF5 files to be used in the density-matrix code. The HDF5 container file format provides a highly flexible and versatile infrastructure to write large amounts of dato into a single file. It takes advantage of the highly parallized architecture of modern high perfomance computers for input and output operations. In an effort to go beyond the dipole approximation in our model of the photoinduced charge carrier dynamics, we use ESP charges to approximate the Coulomb matrix elements that govern the photo-excited processes. The ESP charges are assigned to every atom in the system and their values are fitted to reproduce the electro-static potential of a given dipole transition. We have implemented ESP-charges for finite and extended systems into FHI-aims.

[1] *http://www.hdf5group.org/hdf5*
[2] E. Verdenhalven, *et al.*, Phys. Rev. B **89**, (2014).

S 7

Finding the Ground State: Mixing and Preconditioning

Ville Havu
COMP/Department of Applied Physics, Aalto University, Finland

Search for the density of the electronic ground state and the corresponding potential is a central algorithmic problem in most density functional theory calculations. Due to the nonlinearity of the problem iterative methods must be used. The most popular mixer is the Pulay mixer coupled to a preconditioner of Kerker type. However, several other alternatives exist that can be derived from optimization algorithms or based on physical considerations.

In this talk, we review why certain systems are challenging to converge within the self-consistent field approach, discuss different ways of density mixing and preconditioning, and present solutions for finding the electronic ground state. In addition, we consider methods of optimizing the Kohn-Sham orbitals directly.

S 8

G_0W_0 Calculations based on Non-empirically Tuned Long-range Corrected Hybrid Functionals

Thomas Körzdörfer
Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, Potsdam, Germany

Many-body perturbation theory in the GW approximation is an increasingly popular tool for calculating electron removal energies and fundamental gaps for molecules and solids. Due to the high numerical costs, however, self-consistent GW calculations are bothersome. The most commonly used variant, G_0W_0, calculates a one-shot correction to the eigenvalues obtained from density functionals theory (DFT). The accuracy of the results obtained from $\mathrm{G_0W_0}$ calculations depends strongly on the DFT starting point. While semilocal DFT typically introduces a significant overscreening due to the too small eigenvalue gap, a Hartree-Fock starting point leads to an underestimation of screening effects. Recently, different non-empirical schemes to find a consistent and reliable DFT starting point for $\mathrm{G_0W_0}$ based on global hybrid functionals have been suggested.[1,2] However, these schemes either allow predicting highly accurate photoelectron spectra [1] or highly accurate band gaps and level alignment in donor-acceptor systems such as TCNQ-TTF, [2] but not both at the same time.

Non-empirically tuned long-range corrected hybrid functionals have been suggested as an alternative approach to calculate ionization potentials (IPs) and band-gaps at reduced computational costs as compared to $\mathrm{G_0W_0}$.[3] In these functionals, the range-separation parameter is tuned separately for each system to match the IP-theorem. The IP-tuning procedure can be used to predict very accurate IPs and band-gaps; an extension of this approach to calculate full valence photoelectron spectra has also been discussed.[4,5] Hence, it can be expected that this new class of functionals yields an improved starting point for non-selfconsistent GW calculations compared to semilocal and global hybrid functionals.

We have recently implemented a long-range corrected hybrid functional with ωPBE exchange, PBE correlation, a flexible range-separation parameter (ω), and a flexible amount of global HF-exchange (α) in FHIaims. In this talk, I will introduce our implementation and present the results of the $\mathrm{G_0W_0}$@LRC-ωPBEα calculation of the IPs and EAs of the DNA/RNA nucleobases, several organic acceptor molecules frequently used in organic electronics, and for the level alignment in TCNQ/TTF. The results are compared against several alternative starting points such as semilocal DFT, Hartree-Fock, and global hybrid functionals.[1,2]

[1] T. Körzdörfer and N. Marom, Phys. Rev. B **86**, 041110(R) (2012).
[2] V. Atalla et al., Phys. Rev. B **88**, 165122 (2013).
[3] T. Stein, L. Kronik, and R. Baer, J. Am. Chem. Soc. **131**, 2818 (2009).
[4] S. Refaely-Abramson, et al., Phys. Rev. Lett. **109**, 226405 (2012).
[5] T. Körzdörfer et al., Phys. Rev. B **86**, 205110 (2012).

S 9

Path Integral Molecular Dynamics for Nuclear Static and Dynamical Properties: The i-PI/FHI-aims interface

Mariana Rossi[1], Michele Ceriotti[2], and David Manolopoulos[1]
1: University of Oxford, South Parks Road, OX1 3QZ Oxford, UK
2: EPFL IMX, 338 Bâtiment MXG, CH-1015 Lausanne, Switzerland

At the level of accuracy we can now achieve in first-principles calculations, the inclusion of more subtle nuclear quantum effects (NQE) become more relevant - especially in challenging anharmonic and dynamical systems. Path integral molecular dynamics (PIMD) is the method of choice for including these effects in first-principles simulations of complex materials, due to its favorable scaling with systm size. The i-PI code [1], a python wrapper designed to interface with electronic structure (ES) codes, simplifies the calculation these effects by decoupling the the evolution of the ionic positions to sample the ensemble, and the computation of inter-atomic forces. The final result is a flexible framework where i-PI and the ES code (e.g. FHI-aims) communicate through internet or unix sockets, and the PIMD replicas are trivially parallelizable. Here a short introduction on PIMD and the i-PI interface with FHI-aims will be given. Also, we present a new method based on PIMD, which we call thermostated ring polymer molecular dynamics (TRPMD), for the evaluation of dynamical observables [2]. This method is immune to the pathological problems of both ring polymer molecular dynamics and centroid molecular dynamics, while being analytically just as well defined as RPMD. This method allows for an efficient inclusion of NQE in vibrational spectra and diffusion coefficients, as well as many other dynamical properties.

[1] M. Ceriotti, J. More, D. E. Manolopoulos, CPC **185** 1019 (2013).
[2] M. Rossi, M. Ceriotti, D. E. Manolopoulos, JPC **140**, 234116 (2014).

S 10

From Dispersion Interactions to Farsighted Electron Correlation – A Unified Approach Based on Atomic Response Functions

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

This talk will review the recent developments of efficient methods for an accurate treatment of long-range van der Waals correlation effects in complex molecules and materials. The implementation of these methods in FHI-aims will be highlighted, as well as their applications.

S 11

Using Density Functional Theory to Model Transition States and Long Time Scale Dynamics

Graeme Henkelman and Sam Chill
The University of Texas at Austin

Some recent developments in saddle point finding and long time scale dynamics methods will be presented, possibly including gradient squared minimization; solid state transitions; and basin-constrained molecular dynamics saddle-search based adaptive kinetic Monte Carlo. A discussion of how these methods have been integrated with DFT in the EON software will follow, as well as the possibility of linking to FHI-aims.

S 12

Thermal Conductivity Simulations: Achieving Time and Size Convergence

Christian Carbogno and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

In spite of significant research efforts, a parameter-free first-principles determination of the thermal conductivity at high temperatures, e.g, above 70% of the melting temperature, has remained elusive. Techniques that rely on the harmonic approximation or on small perturbations thereof [1] are questionable in this temperature regime. Similarly, methods based on non-equilibrium molecular dynamics (MD) require enormous temperature gradients along the computationally feasible supercell, and hence lead to undesired non-linear effects [2]. The Green-Kubo method [3], which does not suffer from these shortcomings, involves the assessment of the thermal conductivity from the auto-correlation of the heat flux via equilibrium MD.

We present a first-principles implementation of the Green-Kubo method, in which the non-convective contribution to the heat flux is assessed via the analytical stress tensor. However, achieving time and size convergence can be computationally excruciatingly expensive for systems with low degrees of anharmonicity. We discuss interpolation and extrapolation techniques that allow to overcome these numerical hurdles and demonstrate the general applicability of this approach by investigating the heat transport of zirconia and silicon, two materials that feature particularly low / high thermal conductivities and degrees of anharmonicity.

[1] J. Garg, *et al.*, Phys. Rev. Lett. **106**, 045901 (2011).
[2] P. K. Schelling, S. R. Phillpot, P. Keblinski, Phys. Rev. B **65**, 144306 (2002).
[3] R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Japan **12**, 1203 (1957).

S 13

Density-functional Perturbation Theory for Lattice Dynamics in FHI-aims

Honghui Shang, Christian Carbogno, Patrick Rinke, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

The response of the electronic structure to atomic displacements gives rise to a variety of interesting physical phenomena, which can be probed by experimental techniques such as infrared or Raman spectroscopy or neutron diffraction. The response can be conveniently computed from first principles by means of density-functional perturbation theory (DFPT). Here we present our implementation in the all-electron atom-centered numeric orbital code FHI-aims [1]. Our approach combines the accuracy of an all-electron full-potential treatment with the computationally efficiency of localised atom-centered basis sets that is necessary to study large and complex systems. We verified the accuracy of our DFPT implementation by comparing the vibrational frequencies to finite-difference reference calculations and literature values. Due to the atom-centered nature of the integration grids in FHI-aims, the portion of the grid that belongs to a certain atom also moves when this atom is displaced. Here we demonstrate that, unlike for first derivatives (i.e. forces) [2], this moving-grid-effect plays an important role for second derivatives (i.e. vibrational frequencies). Further analysis reveals that predominantly diagonal force constant terms are affected, which can be bypassed efficiently by invoking translational symmetry.

[1] V. Blum et al. Comp. Phys. Comm. **180**, 2175 (2009)
[2] B. Delley, J. Chem. Phys. **94**, 7245 (1991).

S 14

Structure and Dynamics of Peptide Foldamers from First Principles

Carsten Baldauf, Adriana Supady, Franziska Schubert,
Markus Schneider, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany
Volker Blum
Duke University, MEMS Department, Durham, NC 27708, USA

We study the structure formation and dynamics of peptides and peptide foldamers using first-principles methods,[1] specifically we employ density-functional theory (DFT) corrected for van der Waals interactions. Navigating the conformational space of such flexible (bio-)oligomers is a challenge in itself that we currently tackle with force field based pre-sampling (with basin hopping or replica-exchange molecular dynamics) and then complement with extensive DFT calculations. We compare our results to actual gas-phase experiments, i.e., ion mobility mass spectrometry and vibrational spectroscopy (especially to work by K. Pagel at FU Berlin and G. von Helden at FHI Berlin). I would like to cover three topics in my contribution:

With peptides that feature central prolyl-peptide bonds and that model β turns, we studied the effect of monovalent cations on the structure formation. Cations locally disrupt the hydrogen-bonding network and enforce, by favorable electrostatic interactions, otherwise not observed conformations on the peptide's backbone.[2]

Helix formation of peptides Ac-Ala$_n$-LysH$^+$ in the gas phase has been studied for years now.[3] We added a new direction by studying the effect of increased backbone flexibility on the helix forming properties. For that the β peptide Ac-(β^2hAla)$_6$-LysH$^+$ was designed and investigated. We demonstrated for the first time that β peptides from acyclic monomers can form native-like helices (similar to 3_{10}, α, π). At the same time, the stability order of the three helix types seems to be inverted with respect to their natural α peptide counterpart.

Last I would like to briefly introduce our efforts towards a conformational search and sampling approach that is entirely based on DFT and avoids the use of force fields. The performance of the genetic-algorithm search is assessed by comparison to data for capped amino acids (in house reference data, to be published) and two non-natural α/γ hybrid peptides.[4]

[1] C. Baldauf, H.-J. Hofmann. Helv. Chim. Acta 2012 (95), 2348-2383.
[2] C. Baldauf, K. Pagel, S. Warnke, G. von Helden, B. Koksch, V. Blum, M. Scheffler. Chem. Eur. J. 2013 (19), 11224-11234.
[3] M.F. Jarrold. Phys. Chem. Chem. Phys. 2007 (9), 1559-1671.
[4] R. Kusaka, D. Zhang, P.S. Walsh, J.R. Gord, B.F. Fisher, S.H. Gellman, T.S. Zwier. J. Phys. Chem. A 2013 (117), 10847-10862.

S 15

Property Based Cascade Genetic Algorithm Implementation for Efficient Scanning of $(\mathrm{TiO}_2)_n$ Clusters: Structure Matters more than Size

Saswata Bhattacharya and Luca Ghiringhelli
Theory department, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,Berlin-14195, Germany
Noa Marom
Department of Physics and Engineering Physics, Tulane University, 6400 Freret Street, 2001 Percival Stern Hall, New Orleans, LA-70118

Atomic clusters are widely studied because of the unusual and the technologically useful chemical and physical properties of matter at the nano- and subnano-scale. For the necessary unbiased sampling of the potential energy surface of such systems, we have developed a massively-parallel *cascade* genetic algorithm (GA).[1,2] The term "cascade" refers to a multi-stepped procedure where successive steps employ higher level of theory and each of the next level takes information obtained at the immediate lower level. Therefore, an exhaustive GA pre-scanning of possible structures is done by means of a computationally inexpensive, albeit rather sophisticated, reactive force field. The low-energy structures found with this scanning are used as initial guess for a subsequent GA scanning, where the globally optimized total energy is calculated via density-functional theory (DFT) at the hybrid-functional level. All the benchmarking and validations are duly addressed.[2]

There has been considerable interests for the isomers detected experimentally which are usually not the ground state isomers. It has been reported that in photo-emission experiments performed on anions isomers with high electron affinity of $(\mathrm{TiO_2})_{2-10}$ clusters are selectively observed rather than those with the lowest energy.[3] Therefore, with the *cascade* GA-implementation as described above, the scanning of PES for a reasonably large (viz. $\geq 10-15$ atoms) $(\mathrm{TiO_2})_n$ clusters become prohibitively expensive. This is because, unless we expose the whole PES of such system, we are unable to find those selective meta-stable isomers that are having high electron affinity or low ionization potential.

Therefore, here we introduce a novel *cascade* GA approach where we can do a property (e.g. electron affinity, ionization potential, etc.) based search to locate some specific local minima structures of our interest. This approach is not only faster but also more efficient than the conventional GA schemes. The results are tested on $(\mathrm{TiO_2})_n$ clusters (n=2, 3,..., 10, 15, 20). The structural features that enable high electron affinity or low ionization potential are analysed and discussed.[4]

[1] S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, Phys. Rev. Lett. **111**, 135501 (2013).
[2] S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, to be published (2014).
[3] N. Marom, M. Kim, J. R. Chelikowsky, Phys. Rev. Lett. **108**, 106801 (2012)
[4] S. Bhattacharya, L. M. Ghiringhelli, N. Marom (in preparation).

S 16

Localized Resolution of Identity: Accurate and Efficient Evaluation of the Coulomb Operator for Advanced Electronic Structure Methods

Arvid Conrad Ihrig, Jürgen Wieferink, Igor Ying Zhang, Sergey Levchenko, Matti Ropo*, Patrick Rinke, Volker Blum†, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany
**Tampere University of Technology,*
Department of Physics, FIN-33101 Tampere, Finland
†Duke University,
MEMS Department. 1111 Hudson Hall, Durham, NC 27708, USA

A key component for the application of advanced DFT-functionals and high-level correlation methods is the explicit evaluation of the coulomb operator. For numeric atom-centered orbitals, as used in FHI-aims [1], the arising four-center integrals must be solved with the "Resolution of Identity" (RI) [2], which expands basis function products in an auxiliary basis. The commonly used RI, known as "RI-V", expands all basis function products into the complete auxiliary basis. We developed a localized RI-variant ("RI-LVL"), which expands products of basis functions only in the subset of those auxiliary basis functions centered at the same atoms as the basis functions. This localization allows us to split the RI into a set of operations on atom-pairs, which is more efficient than the RI-V for large systems.

We investigated the performance of RI-LVL for HF, MP2, PBE0 and RPA calculations in the S22 test set of weakly interacting dimers. We found that the error relative to RI-V can be controlled in a systematic way by augmenting the auxiliary basis set with additional basis functions of increasing angular momentum. For the example of fully extended polyalanine chains, we show that RI-LVL exhibits a superior scaling with system size, both in terms of computational time and memory requirements. Furthermore, we also show that RI-LVL is applicable to heavy elements as well at the examples of copper and gold clusters. In contrast to light elements, RI-LVL yields accurate results for these systems even without the use of an augmented auxiliary basis.

[1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009).
[2] X. Ren *et al.*, New Journal of Physics **14**, 053020 (2012).
[3] P. Jurečka *et al.*, Phys. Chem. Chem. Phys **8**, 1985 (2006).

S 17

Implementation of Periodic RPA and GW with Numerical Atomic Orbitals

Xinguo Ren
University of Science and Technology of China

Implementing approaches beyond local-density and generalized gradient approximations (LDA/ GGA) with numerical atomic orbitals (NAO) is difficult due to the large number of multi-center integrals involved that have to be evaluated numerically. Using the resolution-of-identity technique, we have implemented several "beyond-LDA/GGA" approaches [1] in the FHI-aims code [2], which enables efficient calculations for molecular systems. However, a straightforward extension of this technique to periodic systems is still prohibitively expensive.

With a recently developed localized RI approximation [3], we have recently carried out a NAO-based implementation of hybrid functionals, the random-phase approximation (RPA), and *GW* for periodic systems. In this talk, I will present the basic algorithm used in our implementation of RPA and GW in FHI-aims. Benchmark results will be shown to demonstrate the accuracy and efficiency of the implementation. The promise and remaining challenges will be highlighted.

[1] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, and M. Scheffler, New. J. Phys. **14**, 053020 (2012).
[2] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comm. Phys. Comm. **180**, 2175 (2009).
[3] J. Wieferink, A. C. Ihrig, I. Y. Zhang, M. Ropo, X. Ren, R. Rinke, M. Scheffler, and V. Blum, to be published.

S 18

Assessment of Density Functionals in FHI-aims: Searching for the Next-generation Density Functional with a Broader Application

Igor Ying Zhang, Patrick Rinke, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

The FHI-aims package[1] includes all popular density functionals: the local-density approximation (LDA), generalized gradient approximations (GGAs), meta-GGAs, and hybrid-(meta)-GGAs. It also includes some advanced orbital-dependent correlation functionals. In addition to the empirical double-hybrid functional XYG3[2] and the parameter-free random-phase approximation (RPA)[3], a sequence of innovative explorations have been carried out in FHI-aims, leading to the development of, for example, the renormalized second-order perturbation theory (rPT2)[4] and screened coupling second-order perturbation theory (SCPT2), and its empirical extension (ZRS2)[5].

Despite the fact that the DFT is the leading first-principles electronic-structure theory, it is still a big challenge to find a functional that provides a uniform accuracy for general purpose. In this talk, an assessment of a hierarchy of density functionals will be presented based on a set of well-established test sets[6] to cover various kinds of chemical situations: i.e. the G2-1 set (atomization energies), the G2RC set (reaction binding energies), RH76 (reaction barrier heights), ISO34 (isomerization energies), and S22 (bio-oriented weak interactions). The basis-set dependence and CPU time usage of various methods will also be discussed using the valence-correlation consistent (VCC) NAO basis sets[7]. The overall accuracy (mean absolute error, max absolute error) against these sets are LDA: (0.587, 3.625) eV, PBE: (0.236, 1.153) eV, PBEsol: (0.350, 2.068) eV, TPSS: (0.217, 0.837) eV, PBE0: (0.167,0.931) eV, HSE06: (0.172,0.982) eV, RPA: (0.137,1.149) eV, rPT2: (0.114,0.671) eV, XYG3: (0.060,0.404) eV, and ZRS2: (0.062,0.246) eV[8]. Some results from full-configuration interaction method in Quantum Monte Carlo framework (FCI-QMC)[9] will also be presented as references for the density functionals examined in this talk.

[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, *Coumput. Phys. Comm.* **180** 2175 (2009).
[2] Y. Zhang, X. Xu, and W. A. Goddard, *Proc. Natl. Acad. Sci. USA* **106** 4963 (2009).
[3] F. Furche, *Phys. Rev. B* **64** 195120 (2001).
[4] X. Ren, P. Rinke, G. E. Scuseria, and M. Scheffler, *Phys. Rev. B* **88** 035120 (2013).
[5] I. Y. Zhang, P. Rinke, and M. Scheffler, to be published.
[6] L. Goerigk, and S. Grimme *J. Chem. Theory Comput.* **7** 291 (2011).
[7] I. Y. Zhang, X. Ren, V. Blum, M. Scheffler, *New. J. Phys.* **15** 123033 (2013).
[8] The NAO-VCC-N4Z basis set is used for functionals from LDA to hybrid-GGAs. For RPA, XYG3, rPT2 and ZRS2, NAO-VCC-N4Z is used for G2-1, G2RC, BH76 and ISO34, while the extrapolation from N4Z and N5Z is used for the S22 set.
[9] G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131** 054106 (2009).

S 19

Self-consistent Many-body Approaches in FHI-aims

Fabio Caruso
Department of Materials, University of Oxford, United Kingdom

In recent years, the GW approximation emerged as a predominant approach to the calculation of (charged) electronic excitations in electronic structure theory. GW is mostly introduced perturbatively (G_0W_0) following a density-functional theory (DFT) calculation. At a higher computational cost, fully self-consistent GW (sc-GW) ameliorates several shortcomings of the G_0W_0 scheme, such as the dependence on the starting point [1]. Moreover, it allows to treat ground-state properties that are unavailable in G_0W_0.

I present an implementation of sc-GW in the FHI-aims code based on the iterative solution of the Dyson equation [2]. The algorithm – based on numeric atom-centered orbitals and the resolution of the identity – can be easily generalized to self-energies with a different functional dependence on the Green function. At self-consistency, the ground-state electron density and total energy are evaluated directly from the Green's function. Through a comprehensive assessment of ground- and excited-state properties of atoms and molecules, I show that sc-GW generally yields more accurate quasi-particle energies as compared to G_0W_0 based on semi-local DFT approximations. By applying this approach to organic charge-transfer compounds – exemplified by a series of prototypical donor-acceptor molecular systems – I demonstrate 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.*, Phys. Rev. B **86**, 081102(R) (2012).
[2] F. Caruso *et al.*, Phys. Rev. B **88**, 075105 (2013).

S 20

Big Data of Materials Science from First Principles – Critical Next Steps

Matthias Scheffler$^{(*)}$
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

Using first-principles electronic-structure codes, a huge number of materials are being studied since some years. The amount of already created data is immense. Thus, the field is facing the challenges of "Big Data", which are often characterized in terms of the ***"four V"***: **V**olume (amount of information), **V**ariety (heterogeneity of the form and meaning of the data), **V**eracity (uncertainty of the data quality), and **V**elocity at which data may change or new data arrive.

Obviously, the computed data may be used as is: query and read out what was stored. However, for achieving scientific insight, the *four V* need to be complemented by an ***"A"***, the Big-Data ***A****nalysis*. On this branch, big data studies will identify ***correlations*** between putative actuators (descriptors) and the properties of interest. The science starts when the causal inference behind these correlations are revealed and explained.

From the above-mentioned issues, the *4V* & *A*, and for first-principles computational materials science and engineering, the two key challenges concern **big-data *veracity* and *analysis***. These are at the focus of this talk.

(*) work done in collaboration with Luca Ghiringhelli, Jan Vybiral, Claudia Draxl, and Sergey Levchenko

Poster Abstracts

P 1

Curious Case of Vacancies in Thermoelectric Clathrates

Amrita Bhattacharya, Christian Carbogno and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

For the development of novel and improved thermoelectrics, one of the very promising material classes are silicon- and germanium- based type-I clathrates, i.e., Si_{46} or Ge_{46} lattices that encapsulate group I and II metals. In particular, the electronic and phononic transport coefficients that determine the thermoelectric efficiency of such clathrates can be granularly tuned by independently varying the composition of the host and guest lattice [1]. Even in the simplest clathrates, the introduction of guests can result in surprising electronic and structural changes that go well beyond a simple filling of the cages. In the case of a Si-host for instance, synthesis under addition of K results in a K_8Si_{46} clathrate that exhibits metallic behavior due to the electrons donated by the guests [2]. Conversely, Ge-based clathrates retain their semiconducting character [3], since two spontaneously generated tetravalent vacancies ($\square$) balance the surplus electrons stemming from the potassium in $K_8Ge_{44}\square_2$. But even more intriguingly, filling the Ge-clathrate with divalent barium does not generate *four*, but *three* vacancies, whereby the resulting $Ba_8Ge_{43}\square_3$ composition exhibits a curious metal-semiconductor transition at ~ 280 K [4].

In this work, we use density-functional theory as implemented in the electronic structure theory package *FHI-aims* to investigate these puzzling effects. Foremost, we validate our approach by comparing the outcome of calculations performed at different (semi-)local and hybrid levels of theory, e.g., by discussing the impact of the chosen treatment for exchange and correlation on the structural parameters and on the formation energies of diluted defects in type-I clathrates. In a second step, we compute the formation energies for vacancies and vacancy complexes in Si- and Ge-hosts as function of the filling with K and Ba, whereby we take into account structural disorder as well as geometric and lattice relaxations. These calculations unravel the puzzling mechanism that drives/suppresses the spontaneous occurrence of vacancies and thus confirm the experimentally found vacancy concentrations and the associated electronic character of K_8Si_{46}, $K_8Ge_{44}\Box_2$ and $Ba_8Ge_{43}\Box_3$. On the basis of these results, we use the *harmonic* approximation as well as ab initio molecular dynamics to discuss the temperature dependent changes in the electronic and vibrational structure. In the light of our collaboration with the experimental group of M. Baitinger and J. Grin at the MPI for Chemical Physics of Solids, we discuss the implications of our findings for the synthesis of novel thermoelectric materials.

[1] G. J. Snyder and E. S. Toberer, Nat. Mater. **7**, 105 (2008).
[2] G. K. Ramachandran, P. F. McMillan, J. Dong and O. F. Sankey, J. Sol. St. Chem. **154**, 626 (2000).
[3] M. Beekman and G. S. Nolas, Int. J. Appl. Ceram. Technol. **4**, 332 (2007).
[4] U. Aydemir *et al.*, Dalton Trans. **39**, 1078 (2010).

P 2

Predicting the structure of nanoclusters by coupling FHI-aims to KLMC.

Matthew R. Farrow and Scott M. Woodley
University College London, Department of Chemistry,
20 Gordon Street, London, WC1H 0AJ

The prediction of the atomic structure of materials is of fundamental importance. This is particularly true for nanoclusters as they can exhibit substantially different chemical and physical properties compared to bulk phases. The Knowledge Led Master Code (KLMC) [1,2] has been written in FORTRAN90 as a single program that uses MPI and SYSTEM calls in order to automate the many tasks that traditionally a user had to perform by hand. KLMC can call a range of state-of-the-art third party software (TPS) packages including a bespoke library version of the numeric basis set computer program FHI-aims (version 071711_6) [3,4]. Basic examples of tasks KLMC can perform include: creation of input files for TPS; submission of calculations using TPS on either local or external computer platforms; monitoring progress of calculations performed by TPS; extraction of data from TPS output files for use in other KLMC routines or TPS; and, if required, the resubmission of uncompleted jobs (in an appropriate way so as to balance the workload over all available nodes). The evaluation of a set of structures stored as xyz file(s) creation of input files, feeding through the chosen TPS, and collection of energies is, perhaps, the simplest application of KLMC.

In this work, a Lamarckian evolutionary algorithm (EA), implemented within KLMC, successfully located the DFT minima structures of ZnO and MgO nanoclusters. FHI-aims was used to calculate HOMO and LUMO energies, and spectral frequencies of the lowest energy structures for future comparison with experimental data. Using interatomic based pre-screening of candidate structures and Gaussian smearing of electronic energy levels were also investigated as methods for optimising the use of computationally demanding *ab initio* calculations used during the search for atomic structures of nanoclusters. Gaussian smearing of 0.1 eV in the initial geometry refinement steps significantly reduced the number of SCF cycles and, when used in geometry optimisation, this value allowed for hundreds of DFT calculations to be performed on a routine basis. Pre-screening with interatomic potentials was shown to be dramatically more efficient, reducing the number of DFT calculations needed to find the local minima by more than an order of magnitude. Using a suitable functional form of the interatomic potentials, this approach was found to be robust to small changes to the potential parameters.

[1] M. R. Farrow, Y. Chow and S. M. Woodley, PCCP, (2014), DOI: 10.1039/c4cp01825g.
[2] S. M. Woodley, J. Phys. Chem. C, (2013), 117, 24003-24014.
[3] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. G. Ren, K. Reuter and M. Scheffler, Comput. Phys. Commun., (2009),180, 2175
[4] D. Berger, A.J. Logsdail, H. Oberhofer, M. R. Farrow, C. R. A. Catlow, P. Sherwood, K. Reuter, J. Chem. Phys., (2014), 141(2), 024105.

P 3

FHI-aims meets CUDA
GPU acceleration for electronic structure calculations

Björn Lange
Duke University, Mechanical Engineering & Materials Science, Durham, NC 27708-0287, USA
Volker Blum
Duke University, Mechanical Engineering & Materials Science, Durham, NC 27708-0287, USA

Recent compute models predict overcoming the exaflop barrier in 2018. New hardware paradigms such as GPU supported CPUs are a key quantity for breaking this barrier in an energy efficient way. However, this hybrid CPU/GPU hetero structure demands a “changed thinking” for a GPU based implementation of an electronic structure code such as FHI-aims. Here we introduce the programming concept, the interface between the GPU and FHI-aims based on CUDA, and discuss the necessity of load balancing to fairly distribute the workload on the CPU/GPU heterostructure.

P 4

Noncovalent Functionalization with Alkali Metal to Separate Semiconducting from Metallic Carbon Nanotubes: A Theoretical Study

Nannan Li, Jae Won Yang, Jai Sam Kim
Department of Physics, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, Korea
Geunsik Lee, Kwang S. Kim
Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, Korea
Heeyoung Kim, Min Sun Yeom
Department of Application and Support, Supercomputing Center, Korea Institute of Science and Technology Information, 245 Daehak-ro, Yuseong-gu, Daejeon, 305-806, Korea
Ralph H. Scheicher
Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

Despite intense studies of carbon nanotubes for decades, the separation of semiconducting and metallic single-walled carbon nanotubes (SWNTs) remains to be one of the most important tasks to be resolved. Here we demonstrate that a K atom binds the semiconducting SWNTs more strongly than the metallic SWNTs, while this binding strength hierarchy is reversed for a K^+ ion, consistent with experimental reports. This was shown by first-principles calculations, which properly describe the van der Waals interactions, and the origin of such results is explained. These results could be exploited as useful guidance toward separating semiconducting and metallic SWNTs via noncovalent functionalization [1].

[1] Nannan Li et al. J. Phys. Chem. C 117, 4309 (2013).

P 5

Dissecting structures and interactions in polypeptide chains

Mateusz Marianski, Carsten Baldauf, Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

Nowadays, state-of-the-art simulations of biopolymers using Markov State Models [1] or specialized computers [2] can almost reach millisecond time scales, sufficient to study protein structure formation and dynamics as well as ligand binding [3]. However, despite massive computer power that is employed to sample the molecular Free Energy Surface (FES), simulated trajectories suffer from statistical uncertainty [4] and the inaccuracy of the underlying force fields [5].

The presented project aims at the development of kinetic Monte Carlo (kMC) method that is applicable to polypeptide chains and capable of reaching long time dynamics. In general, the kMC scheme requires two components: a list of (all) accessible states and transition rates between them. Since the a priori knowledge of these components requires exhaustive sampling of the FES, instead we approximate the molecular states and transitions of long peptide chains (Ac-Ala$_N$-NMe, N>10) by local kinetics of Markov State Model of short peptide chains (N<5). Effectively, the approximated dynamics encapsulate only the short-range contributions (of varying size) to the overall free energy.

In this contribution, we report that based on fragments of size N=3 80% of the conformations found in exhaustive Replica Exchange MD simulations of Ac-Ala$_{20}$-NMe peptide can be reconstructed. On the other hand, the investigation of free energies of macrostates shows discrepancy between the molecular dynamics, which includes both short- and long-range effects, and the kMC simulations that are currently based solely on short-range interactions.

[1] T. Lane, D. Shukla K. Beauchamp and V. Pande, *Curr. Opin. Struct. Biol.*, **2013**, 23, 58-65
[2] D. E. Shaw *et al.*, *Commun. ACM*, **2008**, 51, 91-97
[3] K. Kohlhoff, D. Shukla *et al.*, *Nat. Chem.*, **2014**, 6, 15-21
[4] Y. Yao, G. Bowman *et al.*, *J. Chem. Phys.*, **2013**, 138, 174106
[5] S. Chutia, M. Rossi, V. Blum, *J. Phys. Chem. B*, **2012**, 116, 14788-804

P 6

Towards First-Principles Modeling of Solvent Effects in Photo-Catalytic Water Splitting

Stefan Ringe, Sebastian Matera, Harald Oberhofer, Karsten Reuter
Chair for Theoretical Chemistry, Technische Universitaet Muenchen, Germany

In the context of solar energy conversion the search for new materials for photo-catalytic water splitting has received new impetus. While in general powerful, computational screening approaches are struggling with the complexity of the underlying physical processes at the solid-liquid interface. Recent work points in particular at the necessity to include at least an efficient description of solvent screening effects to compute meaningful descriptors even in simple computational hydrogen electrode approaches. To this end, we present an implementation of the modified Poisson-Boltzmann (MPB) implicit solvation model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. Optimally integrating into this code environment, we solve the MPB equation in a novel approach based on an expansion of the electrostatic potential in the localized basis functions of FHI-aims. In contrast to common numerical multi-grid solvers this approach can directly make use of the optimized integration schemes used to reach self-consistency and removes the need for numerical interpolation between different grids. We demonstrate the approach and its efficiency for a range of molecular test systems, and show first results for catalytic water splitting on gold nano-clusters.

P 7

The Effects of Golden Mean on the Diffraction by Monatomic One-Dimensional Quasicrystal

Mansur Said
Department of Physics, Northwest University, Kano
G. Babaji
Department of Physics, Bayero University, Kano
S. Abdu
Department of Physics, Kaduna state University

In this work, the code Laue was used to simulate the diffraction pattern and to investigate the effects of varying the golden mean in a monatomic linear quasicrystal having a pseudo atomic potential. The work involved setting the parameters of the code required to simulate the diffraction, running the code and exporting the data generated to excel for analysis. It was found that the shape of the diffraction pattern and the background intensity for a given value of the golden mean is unique. Both the width of the diffraction pattern and the intensity of the central peak decrease with increasing golden mean. Results obtained illustrated the features of the diffraction by quasicrystal and proved the suitability and accuracy of the code in simulating the dynamics of quasicrystals.

P 8

Histidine-cation interaction and microsolvation from first principles

Markus Schneider, Volker Blum[†], Carsten Baldauf, Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany
[†]*Duke University,*
MEMS Department. 1111 Hudson Hall, Durham, NC 27708, USA

Protein-cation interactions may significantly influence the three-dimensional structure of proteins, see *e.g.* [1] or [2]. Of special importance here is the histidine side chain that is, among other examples, involved in the metal cation complexation by the Alzheimer beta-amyloid peptide, see *e.g.* [1]. Our work aims for understanding the binding of cations by histidine as well as its effect on the peptide structure from first principles. However, the first critical point is the appropriateness of the chosen level of theory for quantitative predictions of such interactions. To that end, we focus on the effect of microsolvation, with either zinc or a water molecule or both in competition, on the protonation state of the His side chain. We first assemble a large ensemble of possible conformations from empirical force field calculations. Then, we use these conformations to benchmark the performance of density-functional theory based methods against high-level coupled-cluster calculations. In particular, we assess the PBE [3] generalized gradient approximation as well as the PBE0 [4] and B3LYP [5] hybrid density functionals, all of them corrected for long-range dispersion with either the interatomic pairwise Tkatchenko-Scheffler scheme [6] or a recently improved many-body dispersion scheme (MBD@rsSCS) [7].

[1] K. P. Kepp, *Chem. Rev.* 112 (**2012**), 5193.
[2] C. Baldauf, *et al.*, *Chem. Eur. J.* 19 (**2013**), 11224.
[3] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77 (**1996**), 3865.
[4] C. Adamo, and V. Barone, *J. Chem. Phys.* 110 (**1999**), 6158.
[5] P. J. Stephens, *et al.*, *J. Phys. Chem.* 98 (**1994**), 11623.
[6] A. Tkatchenko, and M. Scheffler, *Phys. Rev. Lett.* 102 (**2009**), 073005.
[7] A. Ambrosetti, *et al.*, *J. Chem. Phys.* 140 (**2014**), 18A508.

P 9

Towards computational solar cell design: Efficiently calculating *ab initio* charge-transfer coupling elements with FHIaims

Christoph Schober, Harald Oberhofer, Karsten Reuter
Chair for Theoretical Chemistry, Technische Universität München, Germany

Organic solar cells promise outstanding application possibilities, but current systems lack the efficiency to be economically viable. Improvements are often the result of experimental intuition or empirical knowledge, rather than strategic design. Towards a computer-aided design we need to understand, amongst others, the complex mechanism of charge propagation in (possibly amorphous) materials.

To this end, Hamiltonian charge-transfer coupling elements are a key ingredient linking microscopic structure and the charge mobilities that determine the device efficiency. To make the calculation of these coupling elements numerically tractable for complex systems we implemented a fragment molecular orbital scheme in FHIaims.[1] Its atom-centered basis set is ideally suited to tackle the non-periodicity of organic solar cell materials efficiently. We use the self-consistent density of the fragments to construct the dimer. Since within FO-DFT no relaxation of the (non-interacting) density is allowed, we can efficiently reduce the final dimer calculation to the construction of the system Hamiltonian, therefore avoiding unnecessary computational overhead. Additionally, we implemented an embedding scheme that allows to consider the generally neglected second fragment and therewith take polarization effects into account. This is achieved by adding the Hartree potential of the neglected fragment as an external potential in the subsequent fragment calculation. We present details on the advantages of calculating coupling elements with FHIaims and compare our calculated charge-transfer coupling elements with the HAB11-set, a database with high quality reference data for coupling elements.[2]

[1] C. Schober, K. Reuter, H. Oberhofer, in preparation.
[2] A. Kubas, et al., *J. Chem. Phys.* 140, 104105 (2014).

P 10

Study of Structural and Electronic Properties of YbAs Compound

Sanjay Kumar Singh*
*School of Studies in Physics, Jiwaji University, Gwalior-474011, Madhya Pradesh, India,*Email : sanjayfizix@gmail.com*
U. P. Verma
School of Studies in Physics, Jiwaji University, Gwalior-474011, Madhya Pradesh, India

In present paper, our aim is to find out the theoretical phase transition pressure, structural and electronic properties of ytterbium arsenide (YbAs) under high pressure by using FP-LAPW+lo method. Hayashi et al.[1] experimentally observed the phase transition properties of YbX(X=P, As, Sb). We have computed ground state properties of ytterbium monopnictides using the full potential linear augmented plane wave plus local orbitals (FP-LAPW+lo) approach within the framework of density functional theory. In the study the generalized gradient approximation (GGA) is chosen for the exchange-correlation functional energy. The local spin-density approximation along with Hubbard-U corrections and spin-orbit coupling has been used for correct prediction of electronic properties. The equilibrium properties viz., equilibrium lattice constants, bulk modulus, its pressure derivative and total energy are calculated in four different phases i.e. NaCl (B1), CsCl (B2), zinc blende (B3), and body centred tetragonal (BCT) phases and compared with previous calculations and available experimental data. At ambient conditions ytterbium arsenide stabilize in NaCl (B1) structure characterized by the space group Fm-3m. Under compression, YbAs undergo first-order structural transition from B1 to BCT phase at 18.21 GPa after that it goes to B2 phase at 21.62 GPa. The LSDA + U method provides better description of electronic properties of present system. The calculation shows YbAs to be semi-metallic in B1 phase while metallic in B2 phase.

[1] J. Hayashi, I. Shirotani , T. Adachi, O. Shimomura and T. Kikegawa. Phil. Mag. 84: 34, 3663, (2004).

P 11

Towards an implicit solvent model for photoelectrochemical processes

Markus Sinstein, Daniel Berger, Harald Oberhofer, and Karsten Reuter
Chair for Theoretical Chemistry, Technische Universität München, Germany
Ran Jia
Institute of Theoretical Chemistry, Jilin University, P.R. China
Volker Blum
Department of Mechanical Engineering and Materials Science, Duke University, United States

Photoelectrochemical systems are widely explored to drive energy-relevant redox reactions like water splitting or CO_2 reduction. The detailed analysis of the involved elementary processes via first-principles calculations is challenged by the necessity to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte. Going beyond the traditionally employed proton-coupled electron transfer mechanism we are furthermore faced with charged intermediate states stabilized by the polar liquid environment. This necessitates a method which captures electrostatic solvent effects whilst being computationally inexpensive in order to allow for an efficient catalyst screening. To this end, we implemented an implicit solvation scheme based on the Multipole Expansion (MPE) method [1] in the DFT package FHI-aims. Within this approach we define the solvent cavity as an iso-density surface which we represent as a collection of points sampled with an efficient restraint dynamics scheme. Finally, we also show early test results of the implicit solvent model.

[1] D. Rinaldi, A. Bouchy, J.-L. Rivail, and V. Dillet, J. Chem. Phys. **120**, 2343 (2004)

P 12

First-principles search for molecular structures with a genetic algorithm

Adriana Supady, Volker Blum[†], Carsten Baldauf, and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft

Faradayweg 4-6, D-14195 Berlin, Germany
[†]*Duke University,*
MEMS Department. 1111 Hudson Hall, Durham, NC 27708, USA

We present a genetic algorithm (GA) based search framework for structural searches of complex molecules based on empirical or first-principles (density-functional theory, DFT) energy functions. The aim is not just to find the single global minimum structure, but also to identify all conformers that appear in the low-energy conformational energy hierarchy and could be experimentally relevant. The use of DFT gives access to rather accurate energy functions and avoids the problem of parameterization for specific classes of chemical compounds. In the GA, the geometry of a structure is encoded in a vector of torsional degrees of freedom (TDOF). The initial population of N individuals is randomly generated and evaluated by local relaxation. Two individuals are selected; the selection probability is a function of energy. Next, genetic operations are applied: (i) crossing over exchanges parts of the encoding vectors and (ii) mutations randomly assign new values to selected TDOFs. The resulting candidate structures are again evaluated by local relaxation and eventually replace individuals of the previous generation with a higher energy. The algorithm proceeds with a new selection round until a predefined number of iterations or a convergence criterion is met. Generated geometries are first checked for steric clashes and uniqueness (that is if they were computed already before) based on root mean square deviation (rmsd) of Cartesian coordinates. This greatly reduces the number of unproductive or redundant calculations, which is especially important when using a first principles energy function. We demonstrate the principle for an azobenzene-based molecule, finding the conformational energy hierarchy for the cis and for the trans configurations. The accuracy of such GA prediction (by means of reproducing the conformational hierarchy from a systematic search) is critically linked to the search settings, for example, the number of repeats. While the global optimum is found very reliably with only a few repeats, the reproduction of the hierarchy is more demanding. Similar testing was performed for seven amino acid dipeptides (Ala, Gly, Val, Leu, Ile, Phe, Trp). Post-processing of the data, for example the evaluation of the geometrical similarity of the structures and taking into account their energetic relation, allows for visualization of the topology of the potential energy landscape in form of a graph. Such information can be further utilized to identify which pairs of states are likely to be connected by a low-energy barrier. We will use the described strategy to predict functional molecules (by adding a library of side groups) that are tuned for a specific use, e.g., as switchable catalysts of a target chemical reaction.

P 13

Introducing mBEEF: An accurate semi-local Bayesian error estimation density functional

Jess Wellendorff, Keld Lundgaard, Aidan Klobuchar, Jens Norskov, Thomas Bligaard
SUNCAT for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA and Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA
Karsten Jacobsen
Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

We have generated a general-purpose meta-GGA density functional [1] within the Bayesian Error Estimation Functional framework [2], and we show how the error estimation ensemble may provide a systematic and quantitative analysis of the reliability of materials property predictions based on DFT.

[1] Wellendorff, Lundgaard, Jacobsen, Bligaard, Journal of Chemical Physics 140, 144107 (2014).
[2] Wellendorff, Lundgaard, Mogelhoj, Petzold, Landis, Norskov, Bligaard, Jacobsen, Physical Review B 85, 235149 (2012).

P 14

Whether ionic carbon dioxide exists at high pressure?

Min Wu
Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5E2
John Tse
Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5E2

Carbon dioxide, as an abundant planetary materials, is extremely important to the study of evolution of earth's interiors as well as other planets like Venus and Mars where it had been found to exist. At high pressure, the phase of carbon dioxide remains in controversial, including an ionic phase which was suggested to be formed at over 85 GPa and can be quenched down to 10 GPa. Our preliminary results show that the ionic phase is not stable and collapses into a disordered structure at 60 GPa. However, more pressure and temperature conditions need to be performed to verify the stability of this ionic phase.

P 15

Sub-Monolayer Water Adsorption on Alkaline Earth Metal Oxide Surfaces: A First-Principles Study

Xunhua Zhao, Saswata Bhattacharya, Luca M. Ghiringhelli, Sergey V. Levchenko and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

The interaction of water with oxide surfaces is ubiquitous in both nature and laboratory, and its understanding is important for the development of novel functional (in particular catalytic) materials. In this work, we predict atomic structures of adsorbed complexes that should appear on alkaline earth metal oxide (001) terraces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory with the hybrid exchange-correlation functional HSE06 combined with the self-consistent many-body dispersion approach [1] is used to calculate total energies. The choice of this functional is validated by renormalized second-order perturbation theory [2]. An unbiased search for global minima of H_xO_y adsorption is performed using first-principles genetic algorithm for periodic models [3]. x and y as a function of temperature and pressure are determined using *ab initio* atomistic thermodynamics.

While isolated water molecules adsorb non-dissociatively on MgO(001) and dissociatively on CaO(001), water-water interaction leads to partial dissociation on both surfaces. Interestingly, we find a range of H_2O and O_2 chemical potentials where one-dimensional adsorbed water structures are thermodynamically stable on CaO(001). This is in a agreement with scanning tunneling microscopy studies of CaO films exposed to water at ultrahigh vacuum conditions[4]. On MgO(001) and SrO(001), thermodynamically stable one-dimensional adsorbed water structures are not found. The formation of the one-dimensional structures on CaO(001) is explained by the balance between adsorbate-adsorbate and adsorbate-surface interactions.

[1] A. Tkatchenko, R. A. DiStasio, Jr., R. Car and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (2012);

[2] X. Ren, P. Rinke, G. E. Scuseria, M. Scheffler, Phys. Rev. B **88**, 035120, (2013);
[3] R. Włodarczyk, M. Sierka, K. Kwapien, J. Sauer, E. Carrasco, A. Aumer, H. J. Freund, J. Phys. Chem. C **115**, 6764, (2011);
[4] X. Shao, N. Nilius, Y. Fujimori, M. Sterrer, and H.-J. Freund, in preparation.

Report on Workshop Density-Functional Theory and Beyond with Numeric Atom-Centered Orbitals

Harnack House of the MPG in Berlin, Germany

August 19 to 22, 2014

sponsored by Psi-k

Christian Carbogno, Carsten Baldauf, Volker Blum, Matthias Scheffler

http://th.fhi-berlin.mpg.de/sitesub/meetings/FHI-aims-2014/

Participants

Overall, this workshop had 47 registered participants, names are listed in the following table.

First name	Family name	Affiliation
Sadiq	Abdu	Kaduna State University
Sebastián	Alarcón Villaseca	Fritz-Haber-Institut der MPG
Alexej	Bagrets	Karlsruhe Institute of Technology
Abdussalam	Balarabe Suleiman	Federal University, Dutse Jigawa
Carsten	Baldauf	Fritz-Haber-Institut der MPG
Susmita	Basak	Fritz-Haber-Institut der MPG
Daniel	Berger	Technische Universität München
Saswata	Bhattacharya	Fritz-Haber-Institut der MPG
Amrita	Bhattacharya	Fritz-Haber-Institut der MPG
Björn	Bieniek	Fritz-Haber-Institut der MPG
Volker	Blum	Duke University, Durham
Christian	Carbogno	Fritz-Haber-Institut der MPG
Fabio	Caruso	University of Oxford
Sam	Chill	The University of Texas at Austin
Woo Jong	Cho	Ulsan National Institute of Science and Technology (UNIST)
Matthew	Farrow	UCL
Lukas	Gallandi	University of Potsdam
Ville	Havu	Aalto University
Graeme	Henkelman	The University of Texas at Houston
Arvid	Ihrig	Fritz-Haber-Institut der MPG
Thomas	Körzdörfer	University of Potsdam
Sanjay	Kumar Singh	Jiwaji University, Gwalior
Björn	Lange	Duke University, Durham
Nannan	Li	Pohang University of Science And Technology
Mateusz	Marianski	Fritz-Haber-Institut der MPG
Aliaksei	Mazheika	Fritz-Haber-Institut der MPG
Christian	Ratsch	UCLA
Xinguo	Ren	University of Science and Technology of China, Hefei
Stefan	Ringe	Technische Universität München
Mariana	Rossi	University of Oxford
Mansur	Said	Northwest University Kano
Matthias	Scheffler	Fritz-Haber-Institut der MPG
Markus	Schneider	Fritz-Haber-Institut der MPG
Christoph	Schober	Technische Universität München
Thomas	Schulthess	ETH Zurich and Swiss National Supercomputing Center

... continued on next page

... continued from previous page

First name	Family name	Affiliation
Honghui	Shang	Fritz-Haber-Institut der MPG
Markus	Sinstein	Technische Universität München
Alexey	Sokol	UCL
Kurt	Stokbro	QuantumWise, Copenhagen
Adriana	Supady	Fritz-Haber-Institut der MPG
Alexandre	Tkatchenko	Fritz-Haber-Institut der MPG
Liudmila	Voronina	Ecole Polytechnique Federale de Lausanne (EPFL)
Jess	Wellendorff	SUNCAT, SLAC National Accelerator Laboratory
Min	Wu	University of Saskatchewan
Jeonghun	Yun	POSTECH, Ulsan
Igor Ying	Zhang	Fritz-Haber-Institut der MPG
Xunhua	Zhao	Fritz-Haber-Institut der MPG