O 51: Focussed Session: Frontiers of Electronic Structure Theory V (jointly with HL and TT)

Time: Wednesday 16:00–19:30　　　　　　　　　　　　　　　　　　　　　　　　　　　　Location: H36

Topical Talk　　　　　　　　　　　O 51.1　Wed 16:00　H36
Screening high throughput density functional theory calculations using simplified models. — •Georg K. H. Madsen, Ingo Opahle, Alessandro Parma, Eunan J. McEniry, and Ralf Drautz — ICAMS, Ruhr Universität Bochum, Bochum, Germany

Thermoelectric materials can be utilized for an efficient conversion of waste heat to electric power. Thermoelectric properties of known compounds can be rationalized and predicted using only the structure as an input.[1] While this can used to discover potential thermoelectric materials by screening known structures[2], there remains a large challenge in discovering unknown phases computationally. Employing a newly developed high throughput environment we show how the stability of binary transition metal silicides can be reproduced using a systematic replacement technique.[3]

As ternary and higher compounds are considered, a combinatorial explosion of potential structures and combinations must be considered. We have therefore develop ed tight binding models of the electronic structure and datamining methods based on the calculation of binary compounds. It will be discussed how these simplified models can be interpreted and used to pre-screen the stability of higher compounds to limit the number of density functional calculations to be done.

O 51.2　Wed 16:30　H36
Tight-binding scale-bridging calculations for steel research — •Nicholas Hatcher, Georg K H Madsen, and Ralf Drautz — ICAMS, Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany

Parameterized methods to extend electronic structure calculations to large systems have recently garnered additional attention due to the limits of traditional DFT. The ability to model low carbon content in steel requires the accurate calculation of millions of atoms. However, interatomic potentials have been shown to be inconsistent with DFT in different environments and cannot give an accurate portrayal of chemical bonding or magnetism. Thus, a coherent transferable tight-binding (TB) parameterization was developed for Fe-C by extracting bonding interactions from DFT and finding a suitable interatomic repulsion. This model gives an accurate description of the energy hierarchy of relevant Fe-C structures, elastic properties, and defect energies. We apply this model to determine mechanisms of carbon segregation to grain boundaries and carbon diffusion in iron, including the interaction of multiple defects under tension and pressure. Furthermore, this intuitive energy functional forms the basis for bond order potentials, thereby extending system sizes to millions of atoms.

O 51.3　Wed 16:45　H36
Local atomic energies from optimal atomic orbitals — •Björn Lange, Christoph Freysoldt, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Deutschland

Decomposing the energy of a condensed matter system into atomic contributions is of great use e.g. for understanding the physical origin of defect and surface energetics or for identifying chemically reactive regions in disordered systems. However, commonly employed energy calculations in the framework of density-functional theory (DFT) do not in general provide a natural decomposition into atoms. Here we propose a novel scheme to achieve this based on the recently introduced concept of atom-centered Quamols[1] that are variationally optimized to represent the electronic structure with a minimal basis set, which largely avoids local overcompleteness issues. The spillage resulting from the remaining small incompleteness is segmented according to a space separation derived from the Quamol atomic densities, maintaining the accuracy of the underlying DFT calculation. The total energy is then decomposed by combining this basis set with a local energy density treatment based on the ideas of Chetty and Martin[2]. We demonstrate the performance of our scheme by visualizing and analyzing the energy distribution at surfaces and in amorphous silicon.

[1] PRB 84, 085101, (2011)
[2] Chetty, N. and Martin, Richard M., PRB 45, 6074, (1992)

O 51.4　Wed 17:00　H36
Environmental linear-scaling tight-binding for multicomponent metallic alloys — •Eunan J. McEniry, Georg K. H. Madsen, and Ralf Drautz — ICAMS, Ruhr-Universität Bochum, Bochum, Germany.

The development of accurate and transferable models to describe the behaviour of multicomponent systems is attracting considerable interest in materials modelling. Tight-binding models derived from density functional theory potentially provide an accurate and systematic approach to this problem. We introduce a methodology for environmental tight-binding (ETB) in which both the overlap and environmental contributions to the electronic structure are included. In order to implement the resulting ETB models within linear-scaling tight-binding approaches, a method for the evaluation of the screening matrix has been developed, based on a Chebyshev expansion of the inverse of the overlap matrix. The resultant linear-scaling environmental tight-binding framework has been applied to a number of relevant material systems, and the transferability and scalability of the approach is discussed. The present contribution outlines our attempts to extend the tight-binding approach towards larger-scale molecular dynamics simulations within a linear-scaling framework.

O 51.5　Wed 17:15　H36
Spontaneous Electric Polarisation from a Classical Perspective. — •Paul Tangney — Imperial College London, London, UK

Spontaneous polarisation is a quantity attributed to noncentrosymmetric crystals and is often associated with a macroscopic electric field permeating the bulk of a sample. Its time derivative is measured as a current density during application of an external stimulus, such as temperature, strain, or an electric field. I will argue that such currents do not require the existence of a spontaneous polarisation field or a macroscopic electric field in the bulk of a polar material. They can be explained by symmetry arguments within a purely classical picture and should be calculable from the time dependence of the many-particle position probability density function of the material's constituent charges - a classical quantity. The only macroscopic electric field across any bulk crystal arises from the charges on its surfaces, which in most cases are strongly influenced by surface relaxation/reconstruction and chemical environment and unlikely to be determined by polarization currents. I will show how the classical picture of polarisation presented is consistent with the Modern Theory of Polarisation[1], in all but interpretation. I will illustrate my arguments with simulations of a toy system.

[1] R. Resta and D. Vanderbilt, "Theory of Polarization: A Modern Approach", in Physics of Ferroelectrics: a Modern Perspective C.H. Ahn, K.M. Rabe, and J.M. Triscone, Eds. Springer-Verlag, (2007).

O 51.6　Wed 17:30　H36
Potential energy surface of BaTiO$_3$ explored with density-functional theory and classical force fields — •Joseph Fallon[1], David McComb[2], Arash Mostofi[1], and Paul Tangney[1] — [1]Imperial College London, London, UK — [2]The Ohio State University, Columbus, USA

Much is known about the electronic structure of BaTiO$_3$, its phonon dispersions, and the energetics of its long wavelength lattice distortions. However, there is much more to learn about the potential energy surface (PES) on which the atoms move. We study the PES using a combination of density functional-theory (DFT) and a polarisable ionic model of interatomic bonding. Our force field is in close agreement with DFT on structures, the PES, and phonon frequencies and allows accurate large scale atomistic simulations of domain structures and dynamics to be performed. A key advantage of an atomistic model over the coarse grained models that are often used to simulate domain dynamics is that it allows the simulation of heterogeneous materials (e.g. grain boundaries, point defects). However, we also point out some features of the PES, which may be important to domain dynamics, that effective Hamiltonians based on the transverse optic soft mode eigenvector and the local strain fail to capture.

O 51.7　Wed 17:45　H36
Efficient Oscillator-Based Approach for Polarizability and van der Waals Interactions — •Vivekanand Gobre[1], Robert A. Distasio Jr.[2], Roberto Car[2], Matthias Scheffler[1], and Alexandre Tkatchenko[1] — [1]Fritz-Haber-Institut der MPG — [2]Princeton University, USA

The dynamic polarizability measures the response to an applied time-dependent electric field, and its accurate determination is crucial for van der Waals (vdW) interactions and other response properties. First-principles calculations of polarizabilities in principle require a computationally expensive explicit treatment of many-electron excitations, and are only applicable in practice to systems with less than about 100 atoms. In this work, we present an efficient parameter-free approach for calculating accurate frequency dependent polarizabilities for molecules with thousands of atoms, as well as periodic materials. This is achieved by the synergistic coupling of the Tkatchenko-Scheffler method [1], which accurately treats short-range hybridization effects, with the self-consistent screening equation from classical electrodynamics [2,3]. Using only the electron density and free atom reference, we obtain an accuracy of 7% for both static polarizabilities and vdW coefficients for an extensive database of gas-phase molecules and crystals. We analyze the interplay of hybridization and long-range screening effects on the polarizability. [1] Tkatchenko and Scheffler, PRL (2009), [2] Felderhof, Physica (1974), [3] Tkatchenko, DiStasio, Car, and Scheffler, PRL (2012).

O 51.8 Wed 18:00 H36

Van der Waals interactions in Density Functional Theory and Linear-scaling Density Functional Theory — •Lampros Andrinopoulos, Nicholas D. M. Hine, and Arash A. Mostofi — Imperial College London, London, United Kingdom

Semilocal functionals in Density Functional Theory (DFT) achieve high accuracy simulating a wide range of systems, but miss the effect of dispersion (vdW) interactions, important in weakly bound systems. We study two different methods to include vdW in DFT: First, we investigate a recent approach [1] to evaluate the vdW contribution to the total energy using maximally-localized Wannier functions. Using a set of simple dimers, we show that it has a number of shortcomings that hamper its predictive power; we then develop and implement a series of improvements [2] and obtain binding energies and equilibrium geometries in closer agreement to quantum-chemical coupled-cluster calculations. Second, we implement the vdW-DF functional [3], using Soler's method [4], within ONETEP [5], a linear-scaling DFT code, and apply it to a range of systems. This method within a linear-scaling DFT code allows the simulation of weakly bound systems of larger scale, such as organic/inorganic interfaces, biological systems and implicit solvation models. [1] P. Silvestrelli, J.P.C. A 113, 5224 (2009). [2] L. Andrinopoulos et al, J.C.P. 135, 154105 (2011). [3] M. Dion et al, P.R.L. 92, 246401 (2004). [4] G. Roman-Perez, J.M. Soler, P.R.L. 103, 096102 (2009). [5] C. Skylaris et al, J.C.P. 122, 084119 (2005).

O 51.9 Wed 18:15 H36

Microscopic van der Waals Interactions with Localized and Metallic States — •Victor Gonzalo Ruiz, Matthias Scheffler, and Alexandre Tkatchenko — Fritz-Haber-Institut der MPG

Several promising methods have been developed in recent years for an efficient modeling of van der Waals (vdW) interactions in molecules and solids. However, essentially all of these methods rely on an localized model for the polarizability, ignoring the rather strong interplay between localized and metallic electronic states. Such states are present in many relevant materials, including transition metals, hybrid organic/metal interfaces, and topological insulators. Here we show how to extend the Tkatchenko-Scheffler method [1] for vdW interactions to treat localized and itinerant electronic states on equal footing by using the gradient of the electron density. In our model, the vdW correction vanishes for the homogeneous electron gas as it should in density-functional theory built upon the local-density approximation. To illustrate the performance of the newly developed microscopic model, we study the cohesive properties of coinage metals and the binding of organic molecules on metals. [1] A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).

O 51.10 Wed 18:30 H36

Self-Consistent Density Functional Including Long-Range van der Waals Interactions — •Nicola Ferri[1], Robert A. Distasio Jr.[2], Roberto Car[2], Matthias Scheffler[1], and Alexandre Tkatchenko[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Princeton University, USA

Van der Waals (vdW) interactions are significant for a wide variety of systems, from noble-gas dimers to complex organic/inorganic interfaces. The long-range vdW energy is a tiny fraction ($\sim$0.001%) of the total energy, hence it is typically assumed that vdW interactions do not change electronic properties. Although the vdW-DF functional self-consistently includes the effect of the vdW energy on electronic structure [1], the influence of "true" long-range vdW interactions is difficult to assess since a significant part of vdW-DF energy arises from short distances. Here, we present a self-consistent implementation of the long-range Tkatchenko-Scheffler (TS) density functional [2], including its extension to surfaces [3]. The analysis of self-consistency for rare-gas dimers allows us to reconcile two different views on vdW interactions: (i) Feynman's view that advocates changes in the electron density, and (ii) atoms separated by an infinite barrier. In agreement with previous work [1], we find the contribution from self-consistency to be negligible in the structure and stability of vdW-bound complexes. However, a closer look at complex organic/inorganic interfaces reveals notable modification of the energy levels when using the self-consistent TS vdW density functional. [1] Thonhauser *et al.*, PRB (2007), [2] Tkatchenko and Scheffler, PRL (2009), [3] Ruiz *et al.*, PRL (2012).

O 51.11 Wed 18:45 H36

Many-Body van der Waals Interactions from Isotropically Damped Coupled Quantum Harmonic Oscillators — •Alberto Ambrosetti[1], Robert A. DiStasio Jr.[2], and Alexandre Tkatchenko[1] — [1]Fritz-Haber institut der MPG, Faradayweg 4-6 14195 Berlin, Germany — [2]Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

The current interest in functional materials with increasing size and complexity demands high accuracy in first-principles calculations. In these systems, the collective many-body (MB) description of van der Waals (vdW) interactions is indispensable to reach the highly coveted "chemical accuracy". The recently introduced DFT+MBD method (PRL **108**, 236402 (2012); PNAS **109** 14791 (2012)) for the dispersion energy based on a coupled set of quantum harmonic oscillators (QHOs) was shown to reach chemical accuracy for gas-phase molecules and molecular solids. Its formulation, however, makes the derivation of interatomic forces and a fully self-consistent DFT+MBD implementation non-trivial. We propose here a simplified approach, making use of a set of QHOs with isotropically damped dipole–dipole coupling, which provides an effective random-phase approximation treatment of their vdW interaction (arXiv:1210.8343). This allows for a simple analytical treatment of interatomic forces, yet providing high efficiency and accuracy. Application over a wide range of systems shows a consistent improvement with respect to pairwise approximations, particularly for the most extended systems.

O 51.12 Wed 19:00 H36

Interplay between H bond symmetrization and spin transition in ϵ-FeOOH: insights from first principles — •Carmen Quiroga and Rossitza Pentcheva — Dept. of Earth and Environmental Sciences, University of Munich

Structural and electronic spin transitions in high-pressure ϵ-FeOOH are studied using density functional theory calculations including an on-site Coulomb repulsion term. A high-spin to low-spin transition in trivalent iron is predicted at $\sim$ 58 GPa, in agreement with previous theoretical study [1] and experimental indications [2]. The spin transition is heralded by a second order $P2_1nm$ to $Pnnm$ phase transition at $\sim$ 43 GPa, driven by hydrogen bond symmetrization at the critical hydrogen bond $O\cdots O$ limit of $\simeq$ 2.4 Å. Our results give indications of a possible connection between the symmetry of hydrogen bonds in ϵ-FeOOH and the spin state of Fe^{3+}, with important implications in disclosing the influence of water content in the mantle redox state.

[1] Otte et al. Phys. Rev. B **80**, 205116 (2009).
[2] Gleason et al. In preparation.

O 51.13 Wed 19:15 H36

From spheres to iso: Implementing implicit solvation in FHI-aims — •Ran Jia, Chunsheng Liu, Daniel Berger, Harald Oberhofer, and Karsten Reuter — Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

At the cost of reduced accuracy, implicit solvation models yield strong speedups compared to explicit solvent simulations. Here, we report on the implementation of the multipole moment expansion (MPE) solvent continuum model into the density-functional theory (DFT) program package FHI-aims. Characterizing the surrounding solvent mainly by its dielectric constant and density, the form of the cavity employed for the solute and the description of the reaction field created by the polarized solvent are the two central characteristics of any implicit sol-

vation approach. In MPE the reaction field is computed as a truncated multipolar expansion. In our implementation we discard the prevalent cavity representation in form of a set of overlapping spheres centered around the solute atoms in favor of an electron isodensity surface. This allows for more flexible shapes with increased physical meaning. In particular, it paves the way towards the description of one- or two-dimensional periodic systems, and therewith to complex solid-liquid interfaces.