

O 26: Methods: Electronic Structure Theory

Time: Tuesday 11:15–12:30

Location: MA 042

O 26.1 Tue 11:15 MA 042

Improved description of correlation energies within an ab-initio framework — •JUDITH HARL and GEORG KRESSE — Vienna University, Sensengasse 8/12, 1090 Vienna, Austria

A well known shortcoming of the standard exchange-correlation functionals (LDA and GGA) used in density functional theory is that they do not include long-range correlation and therefore fail to describe Van-der-Waals bonded systems accurately.

The adiabatic connection fluctuation-dissipation theorem (ACFDT) [1,2] provides an exact expression for the correlation energy depending on the system's response function when switching from the Kohn-Sham to the full many-body Hamiltonian. ACFDT calculations for real systems, mostly within the random phase approximation (RPA), have become feasible recently (e.g. [3,4]).

In this work, we apply the ACFDT within the RPA to rare-gas solids and to a set of insulators and metals. Lattice constants and bulk moduli are improved compared to gradient corrected functionals with relative errors reduced by roughly a factor 2.

[1] D.C.Langreth, J.P.Perdew, *Solid State Commun.* **17**, 1425 (1975).

[2] O.Gunnarsson, B.I.Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).

[3] F.Furche, *Phys. Rev B* **64**, 195120 (2001).

[4] A.Marini *et al.*, *Phys. Rev. Lett.* **96**, 136404 (2006).

O 26.2 Tue 11:30 MA 042

Long-range electronic correlation quantified in rare gas/metal adsorption: Xe/Cu(111). — •MARIANA ROSSI, XINGUO REN, ANDREA SANFILIPPO, PAULA HAVU, VOLKER BLUM, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Berlin, Germany

The adsorption of rare gases on metal surfaces should be a classic example of physisorption, but the underlying electronic binding mechanism remains under debate. Here, we revisit Xe/Cu(111), where empirical potentials predict binding, but the wrong adsorption site (fcc hollow instead of top); in contrast, standard DFT finds the right binding site, but either overbinds significantly (LDA) or hardly binds at all (GGA). To create a systematic picture of binding in this system, we apply the recent local xc correction scheme of Hu, Reuter and Scheffler [1] and a hierarchy of electronic structure approaches of increasing sophistication: LDA, GGA (PBE and BLYP), hybrid functionals, semiempirical C6 corrections for Van der Waals, and MP2, all carried out within the same computational framework, the all-electron code FHI-aims [2]. The inclusion of MP2 is critical to recover the correct Xe binding distance ($d=3.6$ Å). [1]Q. Hu, K. Reuter, and M. Scheffler, *Phys. Rev. Lett.* **98**, 176103 (2007); **99**, 169903(E) (2007). [2] V. Blum *et al.*, The FHI-aims project, www.fhi-berlin.mpg.de/aims/

O 26.3 Tue 11:45 MA 042

On the accuracy of DFT exchange-correlation functionals for H bonds in small water clusters: Benchmarks approaching the complete basis set limit — •BISWAJIT SANTRA¹, ANGELOS MICHAELIDES^{1,2}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany. — ²London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, UK.

The ability of DFT exchange-correlation functionals to describe H bonds between H₂O molecules remains an important open question. Here, we address this issue through a series of studies of small gas phase water clusters. Using Møller-Plesset perturbation theory (MP2) as our reference, we have assessed the abilities of 16 DFT xc functionals to describe the energetics of the low energy isomeric structures of water dimers, trimers, tetramers, and pentamers. Errors from basis set

incompleteness have been minimized in both the MP2 reference data and the DFT calculations, thus, enabling a systematic evaluation of the true performance of the tested functionals. Among the functionals considered, the hybrid X3LYP and PBE0 functionals are the best: predicting H bond strengths within 10 meV (~ 0.3 kcal/mol) of MP2. Of the nonhybrid GGA functionals, mPWLYP and PBE1W perform the best. The popular BLYP and B3LYP functionals consistently underbind. PBE, PW91, and TPSS display rather variable performance with cluster size, leading us to conclude that results from dimers and trimers alone are insufficient to determine the general abilities of a given functional.

O 26.4 Tue 12:00 MA 042

Constrained adiabatic DFT modeling nonadiabatic behavior - simple and effective — •MATTHIAS TIMMER and PETER KRATZER — Fachbereich Physik, Universität Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany

Non-adiabatic effects, in our case the creation of electron-hole pairs, become more and more accessible in theoretical calculations, and they have long been observed experimentally in, e.g., the detection of chemi-currents. We present a new method to calculate the excitation spectrum of electron-hole pairs in adsorption on metals for adatoms which have an initial spin magnetic moment. To accomplish this we use a mapping of the system onto a bosonic Hamiltonian. Starting from adiabatic DFT calculations we calculate the classical trajectory of the adatom. This trajectory can be used to calculate the nonadiabatic occupations of the adiabatic Kohn-Sham states. Nonadiabaticity is originating from spin relaxation effects. In order to describe this relaxation, the spin degree of freedom is treated explicitly within the density matrix formalism. A projection on the adsorbate orbitals is then used to change the occupation of the adiabatic KS states in a way that guarantees the obtained spin polarization localized at the adatom. By treating the spin up and spin down case separately, and by using the density of states, we get separate energy spectra for the spin up and spin down case, and for electrons and holes, which is novel for these computationally fast adiabatic DFT calculations. As an example, we apply our method to the system H on Al(111). We compare our results to previous TDDFT and model calculations.

O 26.5 Tue 12:15 MA 042

Electronic properties of PbTe/CdTe(100) interfaces — •ROMAN LEITSMANN and FRIEDHELM BECHSTEDT — Institut für Festkörpertheorie und -optik, Friedrich-Schiller Universität Jena

Previously studied semiconductor interfaces often consist of chemically different materials with the same crystallographic structure. Usually they are influenced by lattice-constant mismatch and the polarity of adjacent surfaces. Here we investigate the electronic structure of interfaces between highly ionic crystals with different crystal structure but nearly identical cubic lattice constants by first principles total energy calculations in the repeated slab approximation. The interfaces are strongly influenced by electrostatic fields. As a prototypical example we investigate the structural well defined polar PbTe/CdTe(100) interfaces [1,2,3].

We develop four different slab models to calculate the band offsets and projected interface band-structures. These models are used to investigate the electronic properties. The occurrence of interface states is studied versus the different approaches. Moreover we discuss the reliability of the four approaches for the description of different experimental situations.

[1] W. Heiss *et al.*, *APL* **88**, 192109 (2006) [2] R. Leitsmann *et al.*, *New J. Phys.* **8**, 317 (2006) [3] R. Leitsmann *et al.*, *PRB* **74**, 085309 (2006)