

O 84: Density functional theory and beyond for real materials IV

Time: Friday 11:15–13:15

Location: H34

O 84.1 Fri 11:15 H34

Evolution of electron traps at ice surface: aggregation of orientational defects — ●MICHEL BOCKSTEDTE^{1,2}, ANJA MICHL¹, and ANGEL RUBIO² — ¹Theor. Festkörperphysik, FAU Erlangen-Nürnberg, Staudtstr. 7B2, 91058 Erlangen — ²Nano-Bio spectroscopy group and ETSF, Dpto. Física de Materiales, Universidad del País Vasco, Av. Tolosa 72, E-20018 San Sebastián

Water, water clusters and ice possess the fascinating ability to solvate electrons. On crystalline ice long-living solvated electron states were observed that derive from pre-existing surface traps.¹ Theoretical models based on the bi-layer terminated I_h -(0001) relate such traps to orientational defects¹ of the otherwise ordered arrangement of water molecules at the surface.² At these traps with low formation energy, the electron attaches to the local dipole moment of OH-groups pointing out of the surface. In experiments, however, the solvated electron state was found to evolve in a thermally activated process characterized by an enhancement of its binding energy. The underlying reconstruction of the ice-trap is crucial to understand the long life time. Employing density functional theory we address the mechanism of the evolution of the initial trap. We show that an aggregation of orientational defects results in an enhanced localization of the solvated electron. The solvation-triggered aggregation yields structures with an excess energy > 500 meV after the electron detachment. We discuss this mechanism in the light of an alternative evolution via the formation of voids.

[1] Bovensiepen *et al.* J. Chem. Phys. C **113**, 979 (2009).

[2] Buch *et al.* PNAS **105**, 5969 (2008).

O 84.2 Fri 11:30 H34

The role of van der Waals interactions for the cohesive properties of the coinage metals — ●LORENZ ROMANER¹, MATTHIAS SCHEFFLER², and CLAUDIA AMBROSCH-DRAXL¹ — ¹Chair of Atomistic Modelling and Design of Materials, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria. — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany.

Density-functional theory has been successfully applied over many years to calculate binding energies and bond lengths for a wide range of systems. More recently, it has been extended to include long-range correlation interactions and hence could be used for purely van der Waals (vdW) bound systems such as noble gas solids or organic crystals. On the other hand, early calculations for noble metals have revealed a vdW contribution to the cohesive energy [Rehr, Zaremba, Kohn, PRB **12**, 2062 (1975)]. We investigate this issue by employing the vdW-DF approach [Dion *et al.*, PRL **92**, 296401 (2004)], where the exchange interactions are treated within revPBE, and the non-local correlations are based on an approximation to the adiabatic connection formula. We find that the latter give a substantial contribution to the cohesive energies but, overall, vdW-DF underestimates their magnitude while overestimating the lattice parameters. We attribute this shortcoming to the local part of the correlation energy.

O 84.3 Fri 11:45 H34

Ab initio Quantum Monte Carlo: Methods and Applications — ●NORBERT NEMEC^{1,2}, DARIO ALFÈ¹, and RICHARD NEEDS² — ¹University College London, UK — ²University of Cambridge, UK

Quantum Monte Carlo (QMC) methods allow accurate computations of correlated quantum systems. Using a combination of different variants of QMC, the electronic structure of atomistic systems can be handled in ab initio calculations. We present benchmarks on molecules that demonstrate the accuracy and results on graphitic systems that demonstrate intricate finite size effects arising from van der Waals interactions in anisotropic periodic systems.

O 84.4 Fri 12:00 H34

Surface Energies of Transition Metals with Density-Functional Theory and beyond — ALOYSIUS SOON¹, BO LI², MARTIN FUCHS¹, and ●MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²University of California Santa Barbara, California, USA

Determining surface energies of metals is, to date, a great challenge, both theoretically and (even more so) experimentally. Density-functional theory (DFT) calculations of metal surface energies within

the local-density approximation have provided understanding of qualitative trends. Yet absolute surface energies, in particular of d -metals, exhibit significant uncertainties related to the description of exchange-correlation (XC). A more sophisticated treatment of XC for real metals, beyond present-day gradient-corrected approximations is however still an open challenge. In particular, this requires a careful (re-)analysis of the bonding between metal atoms in the bulk and at the surface in terms of explicitly correlated approaches. Such an analysis is attempted in this paper.

Employing the cluster correction scheme¹, we derive surface energies beyond the (semi-)local DFT, using hybrid-DFT XC functionals as well as higher-level approaches (e.g. exact exchange plus the RPA for correlation – EX+cRPA). We find the surface energies of pristine metals to be poorly described (i.e. largely underestimated by about 30%) by hybrid-DFT XC functionals, while the EX+cRPA provides a promising approach towards describing surface energetics. [1] Q.-M. Hu *et al.*, Phys. Rev. Lett. **98**, 176103 (2007); **99**, 169903(E).

O 84.5 Fri 12:15 H34

Assessing the random phase approximation for weakly bonded molecules — ●XINGUO REN, PATRICK RINKE, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, 14195 Berlin, Germany

The random phase approximation (RPA) to the electronic correlation energy has generated increasing interest in recent years due to several of its attractive features. One of these is the automatic and seamless inclusion of van der Waals (vdW) interactions, which makes the RPA free of limitations that empirical vdW correction schemes may suffer from. However, RPA is still an approximate theory, and the treatment of vdW will not be perfect. In addition, RPA calculations are presently performed non-self-consistently with input orbitals from a preceding Hartree-Fock (HF) or standard density functional theory (DFT) calculation. For a systematic assessment of the RPA's performance for vdW interactions, we applied our recent implementation of the RPA [1] to the molecular S22 benchmark set [2], which comprises 22 weakly bonded complexes of different nature. Different DFT/HF orbitals have been used to demonstrate the orbital dependence of RPA. We observe a systematic underbinding of the RPA in all cases, whereby the amount of underbinding depends noticeably on the input orbitals. A detailed analysis reveals that both the exchange and the correlation part of the RPA contribute to this dependence, but in a somewhat counteracting manner. [1] V. Blum *et al.*, Comp. Phys. Comm. **180**, 2175 (2009). [2] P. Jurečka *et al.*, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

O 84.6 Fri 12:30 H34

A simple construction of the GW approximation for molecules — ●DIETRICH FOERSTER¹, PETER KOVAL², and OLIVIER COULAUD³ — ¹CPMOH, Bordeaux, France — ²CNRS, INRIA (Hiepac), Bordeaux, France — ³INRIA (Hiepac), Bordeaux, France

To model the fundamental processes in organic solar cells where light first generates an exciton that is then separated at the donor acceptor interface is a challenging task and requires an extension of existing computational methods to large aperiodic systems. We chose to extend the LCAO approach to excited states in a simple way by defining a space of dominant functions that spans the space of products with exponential accuracy [1]. Using these functions as a basis, we devised an $O(N^2)$ algorithm for computing the Kohn-Sham response function [2] where N is the number of atoms. Our approach simplifies/accelerates the computation of spectra in TDDFT linear response (see the contribution at this symposium of Dr. P. Koval).

In this contribution, we use our construction of the Kohn-Sham response function to give a simple algorithm for the GW approximation. Our results are only “proof of principle” and the complexity of the calculation must still be reduced.

References [1] D. Foerster, J. Chem. Phys. **128**, 034108 (2008); P. Koval and D. Foerster, Physica Status Solidi, submitted (2010) arXiv:0910.3796. [2] D. Foerster, P. Koval., J. Chem. Phys. **131** 044103 (2009). [3] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).

O 84.7 Fri 12:45 H34

An iterative method for TDDFT of large molecules — ●PETER

KOVAL¹, DIETRICH FOERSTER², and OLIVIER COULAUD³ — ¹CNRS, INRIA (Hiepac), Bordeaux, France — ²CPMOH, Bordeaux, France — ³INRIA (Hiepac), Bordeaux, France

To model the processes in organic solar cells where light first generates an exciton that is then separated at the donor acceptor interface is a challenging task. The first difficulty is the size of the molecules used in such devices and the absence of any translational symmetry. Recently, a fast method for computing of the Kohn-Sham response function [1] in a localized basis set [2] has been developed. The Kohn-Sham response function serves as a building block for TDDFT in linear response, for Hedin's GW approach and for the Bethe-Salpeter equation. In TDDFT, a drawback of our response function is its large memory requirements. Fortunately, electronic excitation spectra can be computed with an iterative method of moderate computational and memory cost. This method is similar to van Gisbergens iterative method [3] but we use our basis of dominant functions and a more systematic iterative technique (bi-orthogonal Lanczos, GMRES) [4]. In this contribution, we present examples of TDDFT electronic excitation spectra of molecules used in organic photovoltaic.

References [1] D. Foerster, P. Koval., J. Chem. Phys. **131** 044103 (2009). [2] D. Foerster, J. Chem. Phys. **128**, 034108 (2008). [3] S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. Comput. Chem. **21**, 1511 (2000). [4] Y. Saad, *Iterative Methods for Sparse Linear Systems*, (Siam, Philadelphia 2003).

O 84.8 Fri 13:00 H34

Hybrid Functionals within the All-Electron FLAPW Method: Implementation and Applications — •MARTIN SCHLIPF, MARKUS BETZINGER, CHRISTOPH FRIEDRICH, MARJANA LEZAIC, and STEFAN BLÜGEL — Forschungszentrum Jülich, Institut für Festkörperforschung and Institute for Advanced Simulation

Density-functional theory is exceptionally successful in describing the properties of molecules and solids. However, the commonly used approximations for the exchange-correlation functional - the local-density (LDA) and generalized gradient approximation (GGA) - fail to describe the band gaps and structural properties of a number of semiconducting and insulating materials. The self-interaction error in LDA and GGA is mainly responsible for this shortcoming. It is partly corrected in hybrid functionals, which contain a certain fraction of nonlocal Hartree-Fock exchange. So far, most implementations for periodic systems approximate the presence of the core by pseudopotentials and employ a plane-wave basis set. In this contribution, we present an efficient implementation of the PBE0 and HSE06 functionals within the all-electron full-potential linearized augmented planewave method realized in the FLEUR (www.flapw.de) code. We demonstrate the improvement over LDA and GGA for oxide materials and focus in particular on systems where the results obtained with the standard functionals disagree with experimental results.