O 33: Methods: Electronic structure theory II

Time: Wednesday 10:30–12:00   Location: SCH A316

O 33.1   Wed 10:30   SCH A316

Exploring the Interaction between Graphene Sheets: a Local xc Correction Study — •ANDREA SANFILIPPO[1], XINGUO REN[1], PATRICK RINKE[1,2], ALEXANDER TKATCHENKO[1], VOLKER BLUM[1], MATTHIAS SCHEFFLER[1,2], and KARSTEN REUTER[1] — [1]Fritz-Haber-Institut, D-14195 Berlin (Germany) — [2]UC Santa Barbara, CA 93106 (USA)

The interaction between two graphene sheets has become an important test case when assessing the performance of approximate treatments of electronic exchange and correlation (xc) in the context of van der Waals interactions. Of interest is not only the interaction strength at equilibrium separation, but also the long-range asymptotic behavior, which is expected to be influenced by the half-metallic nature of the graphene band structure. Practical work in this direction is hitherto hampered by existing limitations in applying more sophisticated xc approaches, like correlated wave function techniques, to extended systems. We demonstrate how this can be overcome using a local xc correction formalism [1], which enables an accurate extrapolation of energetics and forces obtained from small cluster calculations. We illustrate this using hybrid functionals, MP2 and the random phase approximation, and compare the obtained ab initio results [2] to analytical predictions for the asymptotic behavior of the electrostatic and dispersive interactions. [1] Q.M. Hu, K. Reuter, and M. Scheffler, Phys. Rev. Lett. **98**, 176103 (2007). [2] V. Blum et al., Comp. Phys. Commun. (in press).

O 33.2   Wed 10:45   SCH A316

Density functional study of the adsorption of Aspirin on (001) surface of α-quartz — •AFSHIN ABBASI[1,2], EBRAHIM NADIMI[1,2], PHILIPP PLÄNITZ[2], and CHRISTIAN RADEHAUS[2,3] — [1]Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany — [2]GWT-TUD GmbH - Geschäftsstelle Chemnitz, Annaberger Str. 240, 09125 Chemnitz, Germany — [3]Fakultät für Elektrotechnik und Informationstechnik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

In this study the adsorption geometry of aspirin molecule on the hydroxylated (001) α-quartz surface has been investigated using DFT calculation. The optimized adsorption geometry indicates that both adsorbed molecule and substrate are strongly deformed. Strong hydrogen bonding between aspirin and surface hydroxyls, leads to the breaking of original hydroxyl-hydroxyl Hydrogen bonds on the surface as well as the covalent bond between aspirin acidic oxygen and hydrogen (O-H). In this case new hydrogen bonds on the hydroxylated (001) α-quartz surface are resulted which significantly differ from ones on the clean surface. The 1.11 eV adsorption energy reveals that the interaction of aspirin with α-quartz is an exothermic chemical interaction. These observations have been used to explain previous experimental results, which had studied the stability of aspirin in the aspirin-silica solid mixtures.

O 33.3   Wed 11:00   SCH A316

Tailoring the electronic properties of LaAlO$_3$ films on SrTiO$_3$(001) via a SrTiO$_3$-capping layer — •KATRIN OTTE[1], ROSSITZA PENTCHEVA[1], and WARREN E. PICKETT[2] — [1]Section Crystallography, Dept. of Earth and Environmental Sciences, University of Munich — [2]Department of Physics, UC Davis

The two-dimensional electron gas emerging at the LaAlO$_3$(LAO)/ SrTiO$_3$(STO) interface [1] is an example of the novel electronic states that can be realized in heterostructures of a polar and a nonpolar band insulator. Recently, Thiel et al. [2] reported a critical thickness of four monolayers (MLs) beyond which the interface of LAO-films on a STO(001) substrate becomes conducting. Using density functional theory (DFT) calculations we demonstrate here that an STO-capping layer can trigger the insulator-to-metal transition already at two MLs of LAO. We have varied both the number of LAO and STO-capping layers and find that already the first STO-capping layer reduces the band gap by 1.2 eV, while additional layers only have a small impact. We identify O2p surface states of alternating p_x, p_y-character as the origin for the band gap collapse. Structural optimization indicates that the lattice polarization in the STO-capping layer has opposite sign to the LAO film.

Altogether, an STO-capping layer represents an alternative pathway to tune the electronic properties of the system with potential for future device applications.
[1] A.Ohtomo and H.Y.Hwang, Nature **427**, 423 (2004)
[2] S.Thiel et al., Science **313**, 1942 (2006)

O 33.4   Wed 11:15   SCH A316

On the accuracy of DFT exchange-correlation functionals for hydrogen bonds in small water clusters — •B. SANTRA[1], A. MICHAELIDES[1,2], and M. SCHEFFLER[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany. — [2]University College London, London, UK.

Recent studies have raised concerns over the ability of DFT exchange-correlation (xc) functionals to reliably describe the structure and properties of liquid water. Hoping to shed light on this issue, we have performed systematic studies of the true ability of several DFT xc functionals to describe hydrogen bonds in small water clusters, making reference to 2nd order Møller-Plesset perturbation theory and diffusion quantum Monte Carlo[1,2]. Errors from basis set incompleteness have been minimized in both the reference data and the DFT calculations. For the total binding energies, the hybrid X3LYP and PBE0 functionals offer the best performance - with absolute errors <10 meV/H$_2$O - and among the pure generalized gradient approximation functionals, mPWLYP and PBE1W perform best. But when the relative energies of different low energy isomers become important, problems with the xc functionals are encountered. Specifically, for the water hexamer, none of the xc functionals tested predict the correct low total energy isomer. Many-body decompositions of the total interaction energies of the clusters indicates that van der Waals forces need to be accounted for in order to correctly discriminate between different isomers with similar energies. The relevance of these results to DFT simulations of liquid water is also briefly discussed. [1] B. Santra et al. J. Chem. Phys. **127**, 184104 (2007). [2] B. Santra et al., J. Chem. Phys. (in press).

O 33.5   Wed 11:30   SCH A316

Subsurface Confinement of Oxygen Vacancies in Anatase TiO2 — •ANNABELLA SELLONI and HONGZHI CHEN — Department of Chemistry, Princeton University, Princeton, NJ-08540, USA.

First principles Density Functional Theory calculations are carried out to study the relative stabilities of oxygen vacancies at surface and subsurface sites of anatase TiO2(101) and TiO2(001) and, for comparison, of the prototypical rutile TiO2(110) surface. Our results show that these defects are substantially more stable at subsurface than at surface sites in the case of anatase surfaces, whereas bridging oxygen sites are favored for O-vacancies at rutile TiO2(110). Also, calculations of vacancy diffusion pathways for anatase (101) show that the energy barrier to diffuse from surface to subsurface sites is sufficiently low to ensure a rapid equilibration of the vacancy distribution at typical surface annealing temperatures. These results can explain why experimentally anatase surfaces are found to have a significantly lower defect concentration and/or to be more difficult to reduce than those of rutile.

O 33.6   Wed 11:45   SCH A316

Trapping of electrons on ice surfaces: an ab initio study — •M. BOCKSTEDTE[1,2], F. BALETTO[3], S. SCANDOLO[4], and A. RUBIO[2,5] — [1]Lst. Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Erlangen, Germany — [2]ETSF, Universidad del Pais Vasco, San Sebastian, Spain — [3]Physics Department, King's College, London, UK. — [4]The Abdus Salam International Center of Theoretical Physics (ICTP) and INFM/Democritos National Simulation Center, Trieste, Italy. — [5]Centro Mixto CSIC-UPV/EHU, San Sebastian, Spain.

Water, water clusters and ice possess the fascinating ability to bind and solvate excess electrons. On crystalline ice films on Ru(0001) a long-living excess electron state was found.[1] The electron resides in pre-existing traps at the surface and shows a continuous energy relaxation on a time scales from femtoseconds to minutes. The nature of the initial trap site and its evolution is an open question. Within the frame work of density functional theory we address prototypical trapping sites for the excess electron on (0001) surface of hexagonal ice (I_h). As the primary traps we identify admolecules, orientational defects and reconstructed orientational defects that have sufficiently low formation energy to explain the experimentally deduced abundance of

trapping sites. The electron binds to the dipole moment resulting from H-O groups oriented towards the vacuum and is entirely localized in front of the surface. Its tunneling into the metal is thus sufficiently suppressed to allow for an enhancement of the screening by thermally activated reconstruction of the ice network around the trap.

[1] Bovensiepen *et al* J. Phys. Chem. in print.