MM 7: Computational Materials Modelling II

Time: Monday 14:30–15:30 Location: IFW B

MM 7.1 Mon 14:30 IFW B

Alkane Adsorption in Chabazite - Different Ways to Model Van Der Waals Interactions — •Florian Göltl and Jürgen Hafner — Faculty for Physics, University of Vienna, Austria

In this work we investigate the performance of different levels of theory to describe the adsorption of alkanes in chabazite, a mineral from the zeolite family. Modeling this problem is an especially challenging task, since, even though there is a very weak bond between the adsorption site (in our case an H- or Na- atom) and the alkane, the bonding is dominated by van der Waals (vdW) interactions between the alkane and the zeolite wall.

Even though vdW-interactions are not included in standard density functional theory (DFT), several ways to include them in DFT and post-DFT methods were proposed. In this work we compare the performance of (i) DFT in its generalized gradient approximation after Perdew, Burke and Ernzerhof (PBE), (ii) PBE with an added force-field after Grimme (PBE-d), (iii) the van der Waals density functional after Dion et al. (vdW-DF), (iv) the Adiabatic Connection Fluctuation Dissipation Theorem in its Random Phase Approximation (RPA), (v) a modified form of the RPA, where the Hartree Fock exchange-contribution is evaluated selfconsistently (RPA-HF) and (vi) 2nd order Møller Plesset perturbation theory (MP2).

We give a critical discussion of differences in structural parameters, charge distribution and energetics and propose an improved way to compare the theoretically obtained results with experiment.

MM 7.2 Mon 14:45 IFW B

Dispersion interactions in room-temperature ionic liquids: Results from a non-empirical density functional — •Carlos Pinilla[1], Emilio Artacho[2], Jose Soler[3], Tristan Youngs[4], and Jorge Kohanoff[4] — [1]ICTP, Strada Costiera 11, 34151, Trieste, Italy — [2]Dept. Earth Sciences, University of Cambridge, CB2 3EQ, UK — [3]Universidad Autonoma de Madrid, Cantoblanco, Spain — [4]ASC, Queens University Belfast, BT7 1NN, UK

The role of dispersion interactions in imidazolium-based room-temperature ionic liquids is studied within the DFT framework, using a recently developed non-empirical functional[1], as efficiently implemented in SIESTA[2]. We present results for the equilibrium structure and lattice parameters of several crystalline phases, finding a general improvement with respect to LDA and GGA. In particular, equilibrium volumes reproduce experimental values to unprecedented accuracy. Intra-molecular geometries are retained, while intermolecular distances and orientations are improved relative to LDA and GGA. The quality is superior to that from tailor-made empirical VDW corrections. We provide some insight into the issue of polymorphism of [bmim][Cl] crystals, and present results for the geometry and energetics of [bmim][Tf] and [mmim][Cl] clusters. By comparing to quantum chemical MP2 calculations on clusters, we validate VDW geometries and binding energies. Finally, we also analyze the performance of an optimized version of this functional[3]. [1] M. Dion et al. Phys. Rev. Lett. 92(2004).[2] G. Román-Pérez et al. Phys. Rev. Lett. 103(2009).[3]J. Klimes, D. et al. J. Phys.:Cond. Mat. 22(2010)

MM 7.3 Mon 15:00 IFW B

Treatment of strongly correlated systems within the framework of reduced density matrix functional theory — •Sangeeta Sharma, J. K. Dewhurst, and E. K. U. Gross — Max-Planck-Institut für Mikrostrukturphysik, D - 06120 Halle

One of the most dramatic failures of the usual local density approximation or generalized gradient type approximations to the exchange-correlation functional of density functional theory is the incorrect prediction of a metallic ground state for the strongly correlated Mott insulators, of which transition metal oxides (TMOs) may be considered as prototypical.

In the present work we extend reduced density matrix functional theory (RDMFT) to the case of solid-state systems and introduce a new functional for their accurate treatment [1]. Furthermore, a method for calculating the spectrum of extended solids within RDMFT is presented. An application of this method to the strongly correlated TMOs demonstrates that (i) an insulating state is found in the absence of magnetic order and, in addition, (ii) the interplay between the charge transfer and Mott-Hubbard correlation is correctly described. In this respect we find that while NiO has a strong charge transfer character to the electronic gap, with substantial hybridization between t_{2g} and oxygen-p states in the lower Hubbard band, for MnO this is almost entirely absent [2]. References 1. S. Sharma, J. K. Dewhurst, N. N. Lathiotakis and E. K. U. Gross Phys. Rev. B 78, 201103 Rapid Comm. (2008) 2. S. Sharma, S. Shallcross, J. K. Dewhurst and E. K. U. Gross cond-mat/0912.1118

MM 7.4 Mon 15:15 IFW B

Understanding Macroscopic Fiber Systems with Statistical Mechanics Concepts — •Nava Schulmann — Institut Charles Sadron, Strasbourg, France

Many natural systems such as cellulose fibers, hair, DNA, or manufactured materials like ropes or wires are made from fibers. The mechanical and statistical mechanic behavior of individual fibers is now well understood and can be described by the physical concepts of torsion, extension and curvature rigidities, and by the topological concepts of twist and writhe. The properties of matter made by many interacting microscopic fibers have also been investigated to some extent, particularly in the limit where fiber rigidity is small enough for thermal forces to play a predominant role. Macroscopic or more rigid systems, where temperature plays a negligible role are much less understood. We have studied fiber stacks [Europhys. Let., 2003, 64, 647], and shown that statistical physics concepts from the thermal systems can be used to understand many properties of the macroscopic systems. In particular, we have shown that the frozen curvature heterogeneities give rise to an effective temperature that controls material properties such as stack compressibility or assembly shape. The aim of this project is to confront the mean-field theoretical predictions for nearly-aligned fiber stacks with numerical simulations. In particular, we want to understand the accuracy of the effective temperature analogy and the limits of the mean-field approximation.