O 65: Density functional theory and beyond for real materials III

Time: Thursday 10:30–13:15 Location: H34

O 65.1 Thu 10:30 H34

Mott transition and Mahan exciton in MgO and ZnO from first principles — •ANDRÉ SCHLEIFE, CLAUDIA RÖDL, FRANK FUCHS, KARSTEN HANNEWALD, and FRIEDHELM BECHSTEDT — Institut für Festkörpertheorie und -optik, Jena, Germany

Under the name "Transparent Electronics" a field is emerging, which already attracted interest, mainly due to the demand for transparent conducting materials for solar cells. Driven by the next generation of optoelectronic devices it is expected to grow even further.

Especially important in this context are the transparent conducting oxides. To combine transparence and conductivity, free carriers have to be present in the conduction bands of these semiconducting materials, which in turn affects the optical properties.

We approach this topic from the theoretical point of view: the solution of the Bethe-Salpeter equation is perfectly suited to describe the optical properties of a system. With this method we gain insight into the optical properties of a system from first-principles and obtain a quantitative understanding of the interplay of additional free carriers and many-body effects.

After introducing our approach along with necessary approximations and technical tweaks, we present results for MgO and ZnO taking into account the influence of an additional free electron gas by including Thomas-Fermi screening and Pauli-Blocking. We relate the resulting effects in the absorption spectrum to the Fermi-edge singularity or Mahan excitons. The comparison with experimental spectra is excellent, but the Mott transition of the excitons is difficult to observe.

O 65.2 Thu 10:45 H34

Unravelling the enigma of the F center in MgO with many-body perturbation theory — •PATRICK RINKE[1,2], ANDERSON JANOTTI[2], ANDRE SCHLEIFE[3], EMMANOUIL KIOUPAKIS[2], CLAUDIA ROEDL[3], FRIEDHELM BECHSTEDT[3], CHRIS G. VAN DE WALLE[2], and MATTHIAS SCHEFFLER[1,2] — [1]Fritz-Haber-Institut der MPG, 14195 Berlin, Germany — [2]Materials Dep., University of California Santa Barbara, CA, USA — [3]Friedrich-Schiller-Universität Jena, 07743 Jena, Germany

The anion vacancy in bulk MgO (also called F- or color center) can probably be regarded as *the* classic intrinsic point defect in compound insulators. Its characterization has been impeded for decades by the fact that the neutral and the positively charged F-center (denoted F and F^+, respectively) absorb at nearly identical energies [1]. To unravel this problem we apply a recently developed formalism that combines density functional theory (DFT) with many-body perturbation theory (MBPT) in the G_0W_0 approximation [2,3]. We find that this approach corrects the DFT formation energies in the local-density approximation (LDA) significantly. To describe the optical spectrum, however, it proves to be necessary to go one step further in the hierarchy of MBPT, i.e. solving the Bethe-Salpeter equation. After inclusion of the electron-hole and electron-phonon interaction we observe unprecedented agreement between the calculated and the experimental optical absorption spectra for the F and F^+ center [1]. [1] L. A. Kappers, *et al.*, Phys. Rev. B **1**, 4151 (1970). [2] Hedström *et al.* Phys. Rev. Lett. **97**, 226401 (2006). [3] P. Rinke, *et al.*, Phys. Rev. Lett. **102**, 026402 (2009).

O 65.3 Thu 11:00 H34

Atomic-level elucidation of the initial stages of self-assembled monolayer metallization — •JOHN KEITH and TIMO JACOB — Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Germany

Developing high performance nanotech applications and molecular electronics requires deep understanding of atomic level structural, electronic, and magnetic properties of electrode/molecular interfaces. To clarify the initial stages of interface formation during self-assembled monolayer (SAM) metallization, we used first principles density functional theory (DFT) calculations to study Pd diffusion on top of 4-mercaptopyridine (4MP)-SAMs on Au(111). After distinguishing potential energy surfaces (PESs) for different spin configurations for Pd on the SAM, we find adatom diffusion and expected Ostwald ripening is not possible over the clean 4MP-SAM surface. Pre-adsorption of Pd, however, facilitates Pd diffusion that appears to explain multiple reports on experimentally observed island and monolayer formation on top of SAMs. Furthermore, these diffusions most likely occur by

moving across low-lying and intersecting PESs of different spin states. Vertical diffusion processes were also investigated, and the electrolyte was found to play a key role in preventing Pd permeation through the SAM to the substrate. Initial stages of nanoparticle formation on top of SAMs are presented, as well as their electronic structures.

O 65.4 Thu 11:15 H34

Benzene on Cu(111): Adsorption and Assembly by Lateral van der Waals and Surface-State-Mediated Interactions — KRISTIAN BERLAND[1], •THEODORE L. EINSTEIN[2], and PER HYLDGAARD[1] — [1]Chalmers U. Tech., Sweden — [2]U. Maryland, USA

Combining a van der Waals density functional (vdW-DF) [PRL 92 (2004) 246401] and estimation of lateral vdW and indirect electronic interactions, we study the adsorption, surface diffusion, and lateral assembly of benzene on Cu(111) [KB,TLE,PH, PRB 80 (2009) 155431]. The vdW-DF inclusion of nonlocal correlations changes the relative stability of 8 high-symmetry binding positions and increases the adsorption energy over tenfold. We find that benzene can move almost freely along a honeycomb web of "corridors" linking fcc and hcp sites via bridge sites, consistent with the low diffusion barrier in experiment.

We further present an extended vdW-DF scheme which accounts well for the structural phases of benzene on Cu(111). Experiments show that benzene condenses into two different structural phases: a compact and a sparse phase, both of approximately hexagonal symmetry. The vdW-DF calculations demonstrate that the denser benzene-overlayer phase, with lattice constant 6.74 Å, is due to direct benzene-benzene vdW attraction. The structure of the second, sparser phase, with lattice spacing 10.24 Å, is attributed to the indirect electronic interactions mediated by the well-known metallic surface state on Cu(111). To support this claim, we use a formal Harris-functional approach to evaluate nonperturbatively the asymptotic form of this indirect interaction. Supported by [1]Vetenskapsrådet 621-2008-4346 & [2]NSF CHE07-50334

O 65.5 Thu 11:30 H34

Kohn-Sham potential for spherical fullerenes — •YAROSLAV PAVLYUKH and JAMAL BERAKDAR — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Strasse 4, 06120 Halle, Germany

Majority of the known cage molecules has low symmetry elongated shapes. Fortunately for the theoretical analysis the most stable fullerenes are spherical and highly symmetric. This makes them accessible for electron correlation methods used up to now only for the closed shell atoms. Starting from valence densities from the first principles quantum chemistry calculations we determine accurate Kohn-Sham potentials for icosahedral C_{20}^{2+} and C_{60} molecules. Assuming that the density is N-representable the Hohenberg-Kohn theorem guarantees the uniqueness of such potential. The potential is iteratively constructed following the method suggested by van Leeuwen and Baerends (Phys. Rev. A **49**, 2421 (1994)). High symmetry of the molecules allows to parametrize angular dependence of the densities and potentials with a small number of symmetry-adapted spherical harmonics. Radially, these quantities are represented on the grid and the density is constructed from the approximate potential by numerically solving the coupled-channel Kohn-Sham equation. This is followed by an update of the potential and the procedure is continued until convergence is achieved.

O 65.6 Thu 11:45 H34

Reliable Kohn-Sham eigenvalues and self-interaction: a study on organic semiconductors — •THOMAS KÖRZDÖRFER and STEPHAN KÜMMEL — Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

Photoelectron spectroscopy is an important tool for investigating organic semiconductor materials such as PTCDA and NTCDA. Kohn-Sham (KS) eigenvalues obtained from density functional theory are frequently used as a tool to facilitate the interpretation of the measured spectra. So far, however, it was difficult to predict when the spectrum of occupied KS eigenvalues obtained from commonly used (semi-)local functionals bears physical relevance and when not. Clearly, this considerably limits the practical usefulness of the approach and triggers the need for an easy criterion which can serve as a warning against possible misinterpretation of the eigenvalue spectrum. In this work,

we demonstrate that such a criterion can be based on evaluating each orbital's self-interaction error [1]. With PTCDA and NTCDA serving as examples it is shown that the spatial structure of the highest lying KS orbitals is decisive for the physical reliability of the eigenvalue spectrum obtained from (semi-)local functionals. We further demonstrate that a recently introduced generalized optimized effective potential scheme [2] that is based on the self-interaction correction of Perdew and Zunger leads to reliable eigenvalues also in difficult cases such as PTCDA where (semi-)local functionals fail.

[1] T. Körzdörfer, et al., Phys. Rev. B 79, 201205(R) (2009).
[2] T. Körzdörfer, et al., J. Chem. Phys. 129, 014110 (2008).

O 65.7   Thu 12:00   H34

A DFT study on electronic structure and vibronic properties of d^8 (Ni-, Pd-, and Pt-) phthalocyanines — •Davoud Pouladsaz[1], Thiruvancheril G. Gopakumar[2], and Michael Schreiber[1] — [1]Institut für Physik, Technische Universität Chemnitz — [2]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel

We studied the HOMO-LUMO gap shrinking in order to investigate the tip-induced polarization in scanning tunneling spectroscopy of d^8 (Ni, Pd, and Pt) phthalocyanines [1]. By means of density functional theory (DFT), the molecular orbital energies have been calculated for Ni-, Pd-, and PtPc single neutral molecules and singly and doubly ionized cations and anions of all molecules. Interestingly, the position of the HOMO decreases systematically with increasing the atomic number of the central metal atom. The first ionization energies of neutral molecules increase by changing the central metal atom, while the electron affinities remain constant. This causes an increase in the HOMO-LUMO gap. These results show a clear correlation to experimental observations. Furthermore, we performed a DFT study on photoelectron spectra of the first and the second ionizations of these molecules, computing the vibronic couplings and the reorganization energies. The partitioning of the reorganization energy into normal mode contributions shows that the major contributions are due to several vibrational modes with a_{1g} symmetry lower than $1600\ cm^{-1}$.

[1] Th. G. Gopakumar, J. Meiss, D. Pouladsaz, and M. Hietschold, J. Phys. Chem. C, **112**, 2529 (2008)

O 65.8   Thu 12:15   H34

Modeling the electronic properties of Pi-conjugated self-assembled monolayers — •Egbert Zojer[1], Ferdinand Rissner[1], and Georg Heimel[2] — [1]Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, A-8010 Graz, Österreich — [2]Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, 12389 Berlin

The modification of electrode surfaces by depositing self-assembled monolayers (SAMs) provides control over various key parameters in organic and molecular electronic devices. These include the work-function of the electrode and the relative alignment of its Fermi level with the conducting states in the SAM and with those in a subsequently deposited organic semiconductor. This contribution summarizes [1] recent progress in developing a proper understanding of the relation between the chemical structure of a molecule, its molecular electronic characteristics, and the properties of a SAM formed by such molecules. This is achieved by linking the insight that can be gained from fundamental electrostatic considerations with a quantum-mechanical description. The roles played by substituents, molecular backbones, chemical anchoring groups, and the packing density of molecules on the metallic surface are elucidated. Also the properties of multilayer structures are addressed. [1] reviewed in: G. Heimel, F. Rissner, and E. Zojer, Progress Report, Adv. Mater., (in print).

O 65.9   Thu 12:30   H34

Charge transport through O-deficient Au-MgO-Au junctions — •Mohamed Fadlallah[1,2], Cosima Schuster[1], Udo Schwingenschlögl[3], Ivan Rungger[4], and Ulrich Eckern[1] — [1]Universität Augsburg, 86135 Augsburg, Germany — [2]Benha University, Benha, Egypt — [3]KAUST, Thuwal 23955-6900, Kingdom of Saudi Arabia — [4]Trinity college, Dublin 2, Ireland

Metal-oxide heterostructures have been attracting considerable attention due to various technological applications as photovoltaic and spintronic devices. We present results of electronic structure and transport calculations for Au/MgO/Au tunnel junctions based on density functional theory and scattering theory on the level of non-equilibrium Green's functions. In particular, we study the dependence of the conductance of the heterostructure on the thickness of the MgO interlayer, the interface termination, and the interface spacing. In addition, we address the effect of O vacancies. The exponential decay with interlayer thickness is modified when Au-O bonds are formed at the interface. Electronic states tracing back to O vacancies change the conductance depending on the position of the vacancy. By increasing the interface spacing, the vacancy induced gap states are shifted towards the Fermi energy, leading to an enhancement of the conductance. Thus, we have identified two mechanisms which determine the conductance of the Au/Mgo/Au-junction: O vacancies are able to increase the transparency of the MgO interlayer; the interface coupling then can be used to fine tune these states.

O 65.10   Thu 12:45   H34

Functionalized Tips Leading towards Ultimate Resolution of Atomic Force Microscopy — •Nikolaj Moll, Leo Gross, Fabian Mohn, Alessandro Curioni, and Gerhard Meyer — IBM Research, Säumerstrasse 4, 8803 Rüschlikon, Switzerland

Ultimate resolution can be achieved by functionalizing the tip with a molecule like carbon monoxide with the tip molecule significantly contributing to the measured force. The force and therefore the resolution crucially depends on the chemical nature of the terminating tip molecule. In this work molecules such as pentacene are imaged with unprecedented resolution by employing such functionalized tips. The interactions of the tip molecule with imaged molecule are studied with ab initio density functional theory (DFT) calculations. The calculations show that Pauli repulsion is the source of the high resolution, whereas van-der-Waals and electrostatic forces only add a diffuse attractive background. This enhancement of the resolution is also observed experimentally and compares very well with the theoretical findings.

O 65.11   Thu 13:00   H34

Yttria stabilized Zirconia: A first principles study — •Christian Carbogno[1], Hepeng Ding[2], Feng Liu[2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany — [2]Department of Materials Science and Engineering, University of Utah, Salt Lake City, USA

Yttria-stabilized Zirconia is widely used in a variety of different technological fields, for instance as a thermal barrier coating in turbine engines due to its extremely low thermal conductivity. Although it is still a topic of scientific debate, it is generally presumed that its macroscopic properties are strongly related to the dynamics of the occurring oxygen vacancies that are induced due to charge compensation by the aliovalent substitutional doping with Yttrium. Previous ab initio studies (e.g. [1]) were able to shed some light on the complex interactions of these vacancies, but the exact mechanism determining the dynamic processes and thus the thermodynamic properties of this ceramic could not be identified by first principles. By exploiting the availability of massively parallel linear-scaling DFT codes [2] we overcome the numerical limitations affecting these previous studies and thus lay the basis for further multi-scale ab initio studies: We investigate how various fundamental properties of Yttria-stabilized Zirconia depend upon the employed exchange-correlation functional and additionally discuss the implications of these results on the simulation of the thermodynamics of the crystal by inspecting the phonon free energies.

[1] F. Pietrucci et al., Phys. Rev. B 78, 094301 (2008).
[2] V. Blum et al., Comp. Phys. Comm. 180, 2175 (2009).