

HL 73: Electronic-Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - VI

Time: Thursday 10:30–13:45

Location: GER 38

HL 73.1 Thu 10:30 GER 38

Implicit solvation functionality in FHI-aims: Kirkwood multipole expansion model — ●MARKUS SINSTEIN, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München, Germany

Implicit solvation models describe a liquid environment in form of a dielectric continuum. Used within first-principles calculations for the solute such models provide a numerically most efficient way to effectively capture solvation effects. To this end we have implemented the multipole expansion (MPE) model introduced originally by Kirkwood into the full-potential density-functional theory (DFT) code FHI-aims. This implementation fully exploits the optimized multi-center multipole decomposition of the density performed within FHI-aims and therewith leads generally to an insignificant overhead as compared to the underlying DFT calculation for the solute.

Aiming to minimize the number of free parameters inevitably connected with such implicit models, we use an iso-density definition of the solvent cavity. As to the other parameters, we present an efficient parametrization scheme based on experimentally measured hydration energies of small organic molecules. Finally, we discuss extensions of the solvation model to address extended solid-liquid interfaces.

HL 73.2 Thu 10:45 GER 38

Using Dispersion-Corrected Density Functional Theory to Understand the Phase Diagram of Alkanethiolates on Gold — ●JOAKIM LÖFGREN, HENRIK GRÖNBECK, KASPER MOTH-POULSEN, and PAUL ERHART — Chalmers University of Technology, Gothenburg, Sweden

A key challenge in modern computational materials chemistry is the description of van der Waals interactions in density functional theory simulations, where the failure of conventional exchange-correlation functionals is well-known. While, in the recent years, several methods have been proposed for overcoming these difficulties, the applications are becoming increasingly more demanding as well. An important example is that of ligand-protected nanoparticles, which typically feature metallic, covalent as well as dispersive interactions that should all, ideally, be treated on an equal footing. In this work we show that significant progress can be made in this direction: with the aid of the recently-developed vdW-DF-cx functional we study the phase diagram of self-assembled monolayers of alkanethiolates on gold. This system is important for practical applications and as a general representative of self-assembly at a metal surface. In particular, a quantitative description of the dispersion-driven phase transition between a lying-down and a standing-up monolayer is obtained using an ab initio thermodynamics framework. The results are shown to be in good agreement with experimental data and highlight that accurately accounting for dispersive interactions is both feasible and a crucial part of modeling self-assembled systems.

HL 73.3 Thu 11:00 GER 38

Finite-temperature properties of the thermoelectric clathrate $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ — ●MARIA TROPPEZ, SANTIAGO RIGAMONTI, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin

Intermetallic clathrate compounds are promising candidates for high-efficiency thermoelectric (TE) applications. Here, we study $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ in the composition range $x \in [6, 16]$ [1]. Recent theoretical studies [2] show a strong dependence of the electronic properties on configuration, i.e. the atomic arrangement of the substitutional Al atoms in the crystal framework. At the Zintl composition ($x=16$), the ground-state configuration is semiconducting. However, configurations higher in energy are metallic. Understanding this metal-semiconductor transition is essential, as semiconducting behavior is a prerequisite for TE applications. In this work, we employ the cluster expansion technique combined with Monte-Carlo simulations and the Wang-Landau method [3] to access finite-temperature properties. We find that the transition is driven by a partial order-disorder transition of the substituents. Most importantly, it is found that the transition temperature (~ 800 K) at the Zintl composition is close to the typical temperatures at which the figure of merit of TE clathrates is maximal. Signatures of the transition in the entropy, order parameter, specific heat, and canonical distribution are analyzed for the full composition range.

[1] J. H. Roudebush *et al.*; *Inorg. Chem.* **51**, 4161 (2012)

[2] M. Troppenz, S. Rigamonti and C. Draxl; preprint.

[3] F. Wang and D. P. Landau, *Phys. Rev. Lett.* **86**, 2050 (2001)

HL 73.4 Thu 11:15 GER 38

Electronic structure and solid-state optical properties of indigo from time-dependent optimally tuned range-separated hybrid functional theory — ●BERND KOLLMANN¹, ARUN KUMAR MANNA², DANIEL LÜFTNER¹, LEEOR KRONIK², and PETER PUSCHNIG¹ — ¹Institute of Physics, NAWI Graz, University of Graz, Austria — ²Department of Materials and Interfaces, Weizmann Institute of Science, Israel

Indigo is a natural dye with a long history in organic chemistry. Recent applications of indigo as a functional building block for organic electronics, like in solar cells or field effect transistors, have renewed the interest in the chemical and physical properties of this molecule. We report on its electronic structure for the isolated molecule as well as for the alpha- and beta- bulk molecular crystal phases. Further we investigate the optical properties of the bulk molecular crystal phases. For the molecule we employ an optimally tuned range-separated hybrid functional (OT-RSH) within density functional theory. Comparing the theoretical results obtained with different levels of theory and with experiment emphasizes the need for going beyond simple semi-local DFT-functionals in order to obtain the correct orbital ordering. For the bulk crystals we take into account the screening in the bulk by using an optimally tuned screened range-separated hybrid (OT-SRSH) approach. Regarding the optical properties of the bulk molecular phases we employ time-dependent density functional theory (TDDFT) to calculate the absorption spectra, whereby TDDFT represents an accurate low-cost substitute to many-body perturbation theory.

HL 73.5 Thu 11:30 GER 38

Thermodynamic properties from ab-initio calculations - Ti as a case study — ●GUY MAKOV — Materials Dept, Ben-Gurion University of the Negev, Beer Sheva, Israel

Ab-initio calculations of thermophysical properties and of phase stability as a function of pressure and temperature are considered in titanium as a case study. Ti is of interest due to its multiple phases and unusual thermophysical properties. At low temperatures Ti has been reported to exhibit negative anisotropic thermal expansion. In addition, there have been reports of two additional phases at high pressure and room temperature, and a possible transition to a bcc phase at very high pressures.

Despite extensive studies there remains both experimental and theoretical uncertainty in determining the phase diagrams and selected properties. Density Functional Theory total energy calculations complemented by Density Functional Perturbation Theory (DFPT) calculations of phonon spectra are obtained as a function of pressure. The free energy and thermal properties (heat capacity and thermal expansion) of Ti phases, phase equilibria and high pressure phase sequence are determined. The contribution of phonon modes to the thermal expansion is analyzed and the negative thermal expansion is shown to be dominated by negative mode Grüneisen parameters at specific points on the Brillouin zone boundaries. The elastic (Debye) theory for negative thermal expansion is shown to be irrelevant for these phenomena. Uncertainties in the calculated results are discussed in light of experimental observations & motivating further experimental studies.

HL 73.6 Thu 11:45 GER 38

Molecular orbitals in the bismuth perovskites — ●KATERYNA FOYEVTSOVA^{1,2}, ARASH KHAZRAIE^{1,2}, ILYA ELFIMOV^{1,2}, and GEORGE A. SAWATZKY^{1,2} — ¹Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada V6T 1Z1 — ²Stewart Blusson Quantum Matter Institute, Vancouver, BC, Canada V6T 1Z4

The bismuth perovskites SrBiO_3 and BaBiO_3 become superconducting upon hole doping, with the transition temperatures as high as 30 K. The origin of the superconductivity in these compounds has remained unidentified for more than three decades. The BCS mechanism alone is not sufficient to account for such a high T_c due to the small electron-phonon coupling that is being consistently found in numerous experimental and theoretical studies. Further effects must therefore

be of key importance, such as, for example, formation of bipolarons.

In this talk, we will focus on the insulating state of the pristine SrBiO₃. Peculiarly, this state is associated with a structural distortion whereby the Bi-O bonds disproportionate, resulting in a three-dimensional array of alternating small and large BiO₆ octahedra. This "breathing" distortion melts away with doping and is believed to be competing with superconductivity. We will show using DFT calculations that the microscopic state in the pristine bismuthates corresponds to a lattice of frozen bipolarons. More specifically, the holes, intrinsically present in the material, condense pairwise into the A_{1g} -symmetric molecular orbitals formed from the $O-p_{\sigma}$ atomic orbitals of the small BiO₆ octahedra. This is facilitated by the strong hybridization between the $O-2p$ states and the Bi-6s states.

HL 73.7 Thu 12:00 GER 38

Ab initio calculations and strain-dependent scaling of excitons in carbon nanotubes — ●CHRISTIAN WAGNER^{1,3}, JÖRG SCHUSTER², MICHAEL SCHREIBER³, and ANDRÉ SCHLEIFE⁴ — ¹Center for Microtechnologies, TU Chemnitz, Germany — ²Fraunhofer Institute ENAS, Chemnitz, Germany — ³Institute of Physics, TU Chemnitz, Germany — ⁴Department for Materials Science, UIUC, USA

Optical transitions in carbon nanotubes (CNTs) show a strong strain sensitivity, which makes them suitable for optical strain sensing at the nano-scale and for strain-tunable emitters. The origin of this effect is the band-gap change, depending on strain and chirality, which is well explored. However, there is no quantitative model for the strain dependence of optical transitions — as they are subject to strong excitonic effects due to the quasi one-dimensional structure of CNTs.

One approach towards such a model is the scaling relation of CNT excitons with respect to dielectric constant, reduced mass, and CNT radius given by Perebeinos *et al.* However, the description of screening in this model is insufficient, since for CNTs, a one-dimensional wave-vector dependent dielectric function $\epsilon(q)$ is needed instead of an effective-medium dielectric constant ϵ_0 .

We achieve this by combining the scaling relation with the wave-vector dependent screening model by Deslippe *et al.* The strain-dependent scaling is fitted to electronic-structure calculations within many-body perturbation theory as a reference. This enables us to quantitatively predict the strain dependence of optical transitions for any CNT.

HL 73.8 Thu 12:15 GER 38

Dzyaloshinskii-Moriya-interaction energy, where it is located? Real and reciprocal spaces views. — ●LEONID SANDRATSKII — Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Recently Dzyaloshinskii-Moriya interaction (DMI) attracted new wave of intense attention stimulated by its role in the stabilization and fast dynamics of skyrmions. Numerous approaches have been suggested for the estimation of the the DMI parameters. Many efforts are devoted to reveal the electronic properties responsible for the strength of the DMI and, in this way, to help to engineer the materials with desired DMI characteristics. Although there is full consensus with respect to the most fundamental reasons of the DMI, the SOC and broken inversion symmetry, in details the physical pictures suggested by different authors differ strongly. In particular, this concerns the role of the avoiding crossings in the electronic structure, the spatial location of the DMI energy, the role of the orbital moments. This stimulated us to perform detailed study of the DMI in CoPt bilayer focusing on the open questions. We used both the approximate calculations for spin spirals with arbitrary wave vectors and more precise but also more time and resources consuming full relativistic calculations for supercells with the magnetic structures of opposite chirality. The results of the calculations are presented and analyzed.

HL 73.9 Thu 12:30 GER 38

Ab-initio study of the Raman spectra of strained graphene — ●ALBIN HERTRICH, CATERINA COCCHI, PASQUALE PAVONE, and CLAUDIA DRAXL — Department of Physics, Humboldt-Universität zu Berlin, Germany

Raman spectroscopy is an important non-destructive method for characterizing graphene-based materials. The main features of Raman spectra of pristine graphene are the first-order G-band at $\approx 1580 \text{ cm}^{-1}$ and the dispersive second-order 2D-band at $\approx 2700 \text{ cm}^{-1}$. In this work, we perform a systematic analysis on the effect of strain on both bands. All calculations are done using the full-potential all-electron code **exciting** [1]. Phonon properties are computed within

the frozen-phonon approximation, the frequency-dependent dielectric tensor within the random-phase approximation. Raman-scattering intensities are calculated from vibrational matrix elements and derivatives of the dielectric tensor with respect to the phonon normal coordinates [2]. Under biaxial strain both Raman bands are shifted, while uniaxial strain leads to a splitting of the G-band by lifting the degeneracy of the optical in-plane Γ -point phonons. Further, we explore the effect of different types of inhomogeneous strain on the optical phonon frequencies and Raman-scattering intensities.

[1] A. Gulans *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014).

[2] C. Ambrosch-Draxl *et al.*, Phys. Rev. B **65**, 064501 (2002).

HL 73.10 Thu 12:45 GER 38

DFT meets Landau Theory: The High Pressure Phase Transition of Lead Titanate — ●ANDREAS TRÖSTER — Vienna University of Technology, Institute of Material Chemistry, Getreidemarkt 9 A-1060 Wien, Austria

Landau theory (LT) coupled to infinitesimal strain is a cornerstone of the theory of structural phase transitions. At high pressures, however, this approach breaks down due to the appearance of large strains and the accompanying nonlinear elastic energy contributions. In density functional theory (DFT), on the other hand, stress and strain are easy to control, but entropic effects are difficult to incorporate since DFT is a genuine zero temperature method. Recently we have shown how to combine the strengths of these two antipodal approaches by constructing a high pressure extension of conventional LT with the help of DFT. Essential for the success of this approach is the ab initio calculation of pressure-dependent elastic constants. This theory yields a concise numerical description of the high pressure phase transition in strontium titanate, and also allows to resolve a number of severe and long-standing discrepancies between the experimental data and the theoretical description of the ferroelectric high pressure phase transition of the perovskite lead titanate, a material which is also of considerable technological interest.

HL 73.11 Thu 13:00 GER 38

Ground-State and Excitation Properties of Orthorhombic MAPbI₃ — ●CLAUDIA RÖDL and SILVANA BOTTI — Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

Hybrid organic-inorganic halide perovskites are one of the most promising candidates for the next generation of photovoltaic devices with high power-conversion efficiencies. Despite the amazing progress in device fabrication, many of the fundamental properties of these materials are not yet understood. The flexibility in composition of hybrid perovskites permits to tune physical properties like band gap, dielectric constant, or optical absorption which renders them interesting also from a fundamental point of view and for applications beyond photovoltaics. The most intensively studied compound, methylammonium lead iodide (MAPbI₃), condenses in a low-temperature orthorhombic phase which undergoes a phase transition to a tetragonal structure at 162.2 K and transforms into a cubic high-temperature phase above 327.4 K. These phase transitions go along with a change in the optical properties. Here, we focus on the orthorhombic phase of MAPbI₃. We have studied the ground-state atomic structure, and in particular the orientation of the MA⁺ ion within the inorganic cage, within density-functional theory. We investigate the one-particle excitation properties (band gap, photoemission spectrum) within the *GW* approximation of many-body perturbation theory. Moreover, we calculate optical and loss spectra using time-dependent density-functional theory and solving the Bethe-Salpeter equation.

HL 73.12 Thu 13:15 GER 38

Structure, nonstoichiometry, and geometrical frustration of α -tetragonal boron — ●JENS KUNSTMANN¹, NAOKI UEMURA², HAGEN ECKERT¹, and KOUN SHIRAI² — ¹TU Dresden, Germany — ²Osaka University, Japan

It is currently believed that boron in the α -tetragonal structure is not an elemental crystal. Here we contradict this view and resolve the structural and thermodynamic characteristics of pure α -tetragonal boron via density functional theory calculations. The conditions for stable covalent bonding are almost fulfilled at a stoichiometric composition B₅₂. This phase is an elemental crystals with geometrical frustration. Furthermore, our thermodynamic considerations show that small, positive deviations from the stoichiometric composition occur at finite temperatures. [Uemura, Shirai, Eckert, Kunstmann, Phys. Rev. B **93**, 104101 (2016)]

HL 73.13 Thu 13:30 GER 38

Magnetic response properties of thin films using Kubo's linear response formalism — ●ANDREAS HELD, SEBASTIAN WIMMER, SERGIY MANKOVSKY, and HUBERT EBERT — Department Chemie, Ludwig-Maximilians-Universität München

We have applied the fully relativistic spin-polarized Korringa-Kohn-Rostoker method to investigate various magnetic response properties of two-dimensional systems such as free-standing mono- and multilayers, surfaces and thin films on surfaces. Our approach is based on an implementation of Kubo's linear response formalism within the tight-binding (or screened) KKR framework that allows introducing layer-resolved response coefficients τ_{ij}^{IJ} . Extending previous work [1]

focusing on the symmetric part of the electrical conductivity tensor, we are able to describe the full response tensors connected to charge and spin transport, Gilbert damping, spin-orbit torque and the Edelstein effect. An implementation of the Coherent Potential Approximation for layered systems allows the treatment of disorder effects including the Vertex Corrections to the response coefficients [2]. This can be used to study chemical disorder in alloys but also to include the effect of finite temperatures. For the latter the so-called Alloy-Analogy Model [3] is employed to treat vibrations and spin fluctuations.

[1] W.H. Butler *et al.*, *Phys. Rev. B* **52**, 13399 (1995). [2] W.H. Butler, *Phys. Rev. B* **31**, 3260 (1985); K. Palotás *et al.*, *Phys. Rev. B* **67**, 174404 (2003). [3] H. Ebert *et al.*, *Phys. Rev. B* **91**, 165132 (2015).