

HL 40: Focus Session: Frontiers of Electronic-Structure Theory VI (joint session O/HL)

Time: Thursday 10:30–12:45

Location: TRE Ma

HL 40.1 Thu 10:30 TRE Ma

Nailing down charge-density-wave phase-transition temperatures with downfolding approaches — ●ARNE SCHOBERT¹, JAN BERGES², MICHAEL SENTEF³, ERIK VAN LOON⁴, SERGEY BRENER¹, MARIANA ROSSI³, and TIM WEHLING¹ — ¹University of Hamburg, Germany — ²University of Bremen, Germany — ³MPSD, Hamburg, Germany — ⁴Lund University, Sweden

The coupled dynamics of electrons and nuclei is an extremely complex problem of relevance to multiple branches of sciences. *Ab initio* molecular dynamics (AIMD) simulations are often challenging — especially in large systems, on long time scales, in non-equilibrium or in presence of strong correlation. We can overcome these problems by mapping the full *ab initio* density functional theory (DFT) Hamiltonian onto a low-energy lattice model through downfolding. Three different downfolding strategies based on constraining, unscreening and combinations thereof are compared. The best performing model, which properly accounts for anharmonicity, is combined with path integral molecular dynamics (PIMD). This allows us to nail down the transition temperatures of charge-density waves — for instance in 1H-TaS₂.

HL 40.2 Thu 10:45 TRE Ma

Structural and electronic properties of the Ba₈Au_xGe_{46-x} clathrate: an ab-initio study with cluster expansion — ●PETER WEBER, SANTIAGO RIGAMONTI, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Berlin, Germany

Intermetallic clathrate materials are promising candidates for high-efficiency thermoelectric applications as they can reach very low thermal conductivity. These materials possess a cage-like structure containing guest atoms. Their electronic properties can be tailored by exploiting the idea of the phonon-glass–electron-crystal which allows for reaching a large figure of merit. We study the compound Ba₈Au_xGe_{46-x} ($0 \leq x \leq 8$), which has raised interest due to its glass-like thermal conductivity [1]. Using the Zintl concept, a semiconducting state is expected to occur at the charge-balanced composition corresponding to $x=5.33$. This composition requires a supercell of at least 3 unit cells (162 atoms) which makes a direct *ab initio* study challenging. We tackle this problem by using the cluster expansion method combined with density-functional theory calculations. In this way, we are able to find the atomic ground-state configurations, together with various properties at different temperatures and gold content. These include lattice constants, bond lengths, site occupancies, as well as band gaps and band structures which are compared with available experimental data.

[1] P.-F. Lory, *et al.* Nature Communications **8**, 491 (2017).

Topical Talk

HL 40.3 Thu 11:00 TRE Ma

New Opportunities for First Principles Simulations of Thousands of Atoms Using Linear Scaling Density Functional Theory — ●LAURA RATCLIFF — University of Bristol, Bristol, United Kingdom

Density-functional theory (DFT) is routinely used to simulate a wide variety of materials and properties, however, standard implementations are cubic scaling with the number of atoms, limiting the system sizes which can be treated. This motivated the development of alternative implementations of DFT, which exploit the nearsightedness principle by using a localised description of the system, leading to algorithms with linear scaling (LS) cost which can treat large systems containing tens of thousands of atoms. One approach, which is implemented in the wavelet-based BigDFT code, uses localised orbitals, also known as support functions, which are optimised to reflect their local chemical environment, and thus constitute an accurate minimal basis set. Beyond reduced computational cost, the localised support function description also facilitates additional developments, such as the ability to automate a fragment-based description. In this talk we will present the formalism behind LS-BigDFT, including some examples of the new types of systems and analyses which are opened up by the ability to treat such large systems. We will also describe recent developments in PyBigDFT, a python-based interface which aims to simplify the usage of LS-BigDFT for complex systems and workflows.

15 min. break

HL 40.4 Thu 11:45 TRE Ma

Fully Anharmonic Electronic Transport Coefficients from Temperature-dependent Spectral Functions — ●JINGKAI QUAN, MATTHIAS SCHEFFLER, and CHRISTIAN CARBOGNO — The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin

The combination of *ab initio* molecular dynamics (aiMD) and band-structure unfolding techniques provides a non-perturbative route to obtain temperature-dependent spectral functions. [1] In contrast to commonly employed perturbative approaches [2], this technique accounts for all orders of anharmonic and vibronic couplings. Building on this non-perturbative formalisms, we here present an approach to obtain electronic transport coefficient such as the electrical conductivity using Kubo's formulation of the fluctuation-dissipation theorem. By this means, all relevant quantities, including electron lifetimes, are obtained from the unfolded, self-consistent wave functions computed during the aiMD runs. We critically benchmark the approach against existing perturbative data for harmonic systems, carefully analyzing to which extent short- and long-range couplings are captured with increasing supercell size. Furthermore, we demonstrate the advantages of the proposed approach for strongly anharmonic systems, for which perturbative approaches become unreliable.

[1] M. Zacharias, M. Scheffler, and C. Carbogno, *Phys. Rev. B* **102**, 045126 (2020).

[2] F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).

HL 40.5 Thu 12:00 TRE Ma

Accurate prediction of vibrational spectra for solid state systems from ab initio molecular dynamics — ●EKIN ESME BAS, THOMAS HEINE, and DOROTHEA GOLZE — Chair of Theoretical Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

We present a highly accurate computational method to calculate vibrational spectra for solid state materials, primarily for covalent-organic frameworks (COFs). IR and Raman spectra are important tools that are frequently used for material characterization. However, the experimental spectra are often difficult to interpret without aid from theory. The computation of IR and Raman spectra is usually based on the harmonic approximation where molecular vibrations can be determined as normal modes from the second derivatives of the electronic energy with respect to the coordinates. Although this method is more straightforward and computationally less expensive, anharmonic modes cannot be captured. Thus, we employ an AIMD (*ab initio* molecular dynamics) based approach to include vibrational anharmonicities. Power, IR and Raman spectra can then be calculated via a Fourier transformation of the time correlation functions of velocities, dipole moments and polarizability tensors, respectively [1]. We discuss different approaches to compute dipole moments and polarizabilities. We present the power, IR and Raman spectra we calculated for COF-1, and we compare our AIMD based approach to the spectra obtained via harmonic approximation and experiment.

[1] M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner. *Phys. Chem. Chem. Phys.*, 6608-6622, 5, 2013.

HL 40.6 Thu 12:15 TRE Ma

Anharmonic Fingerprints from THz Modes of Polyacene Crystals — ●PAOLO LAZZARONI, SHUBHAM SHARMA, and MARIANA ROSSI — Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Organic molecular crystals exhibit strong lattice anharmonicity, especially in the collective motions that are governed by intermolecular interactions and lie in the low-frequency THz range [1]. Inspired by recent observations that the polarization-orientation (PO) Raman spectra can give exquisite insight into the anharmonic couplings between modes [2], we devise a first-principles framework that can reproduce, explain and give quantitative insight into the type and strengths of mode coupling. This framework is based on machine-learned potentials and polarizability tensors trained on *ab initio* molecular dynamics trajectories [3]. We obtain results through the time-correlation formalism for PO Raman signals, retaining the full anharmonic nature of the potential, and perform a novel analysis of effective temperature-dependent mode couplings from our trajectories. [1] M. Asher *et al.*, *Adv. Mater.* **32**, 1908028 (2020) [2] N. Benshalom *et*

al., arXiv:2204.12528 (2022) [3] N. Raimbault *et al.*, *New J. Phys.* **21** 105001 (2019)

HL 40.7 Thu 12:30 TRE Ma

A first-principles Newns-Anderson chemisorption function applied to ultrafast electron transfer —

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We offer a method to calculate the electronic couplings H_{ad} between an adsorbate and substrate in an ab-initio fashion. The couplings are acquired by projection of the Kohn-Sham Hamiltonian onto a diabatic basis[1]. By averaging over the Brillouin Zone, it becomes possible to calculate a convergent chemisorption function of Newns

and Anderson[2], which gives the energetic broadening of an adsorbate frontier orbital upon adsorption. This broadening corresponds to the experimentally-observable lifetime of an electron in the state, which we confirm for the case of core-excited $\text{Ar}^*(2p_{3/2}^{-1}4s)$ atoms on a number of transition metal surfaces[3].

We find that the (tunneling) model captures and elucidates aspects of energy-dependence, spin, phase cancellation and k-space in the electron transfer process, in particular suggesting a significant role played by the surface d-bands. Given the prevalence of electronic couplings - and the chemisorption function - in theoretical models, we discuss potential for further applications.

[1] S. Ghan et al., *J. Chem. Theory Comput.* **16**, 7431 (2020).

[2] D. Newns, *Phys. Rev.* **178**, 3, 1123 (1969).

[3] F. Blobner et al., *Phys. Rev. Lett.* **112**, 086801 (2014).