# O 11: Electronic Structure Theory

Time: Monday 15:00–16:30  Location: H6

O 11.1  Mon 15:00  H6

**Quantum Nuclear Effects in Thermal Transport of Semiconductors and Insulators** — •Hagen-Henrik Kowalski[1], Matthias Scheffler[1], Mariana Rossi[2], and Christian Carbogno[1] — [1]The NOMAD Laboratory at the FHI-MPG and HU, Berlin, Germany — [2]MPI for Structure and Dynamics of Matter, Hamburg, Germany

Accounting for the nuclear motion is essential for the prediction of various material properties, from thermal conductivity to the relative stability of different polymorphs. Often, it is assumed that quantum nuclear effects (QNEs) are decisive at low temperatures, but that anharmonic effects can be neglected in this limit. Conversely, it is often presumed that anharmonicity is influential at elevated temperatures, but that QNEs are not active in this limit. In this work, we investigate the interplay of QNEs and anharmonicity by extending a recently proposed anharmonicity metric [1] to path integral molecular dynamics (PIMD). Our *ab initio* MD and PIMD calculations for solid Argon, Silicon, Lithium Hydrid, and Pentacene further substantiate that QNEs can have a massive impact even at room temperature and beyond, especially in weakly bonded systems [2]. Furthermore, we show that QNEs can induce strong anharmonic effects –beyond the applicability realm of perturbation theory– even at 0K. We discuss the underlying microscopic mechanisms and hence elucidate why QNEs and strong anharmonicity often go hand in hand in real materials.
[1] F. Knoop, et.al., *Phys. Rev. Mat.* **4**, 083809, (2020).
[2] M.Rossi, *J. Chem. Phys.* **154**, 170902 (2021)

O 11.2  Mon 15:15  H6

**Volume Dependence of Excitation Energies of Sodium Clusters in GW** — •Štěpán Marek and Richard Korytár — Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Prediction of molecular junction transport properties is a challenging task. One particularly complicated aspect of the problem is accurate description of binding between the molecule and the electrodes. Effect of image charges and non-ground state properties of the molecule-electrode system are expected to induce significant error when using DFT to evaluate the junction properties. GW is a post-DFT method that is assumed to fix some of the problems of bare DFT approach. In this contribution, we explore the (size) convergence properties of spectrum of sodium clusters using GW, and compare it to predictions by DFT and HF. We discuss the strategies to remove quasi-degeneracies induced by symmetries of the clusters, and their impact on critical properties of the spectrum, namely gap and average level spacing. Our analysis serves as a guide towards convergence studies of molecular junctions using GW.

O 11.3  Mon 15:30  H6

***Ab initio* phonon self-energies: To screen, or not to screen** — •Jan Berges[1], Nina Girotto[2], Tim Wehling[3], Nicola Marzari[4,1], and Samuel Poncé[5] — [1]University of Bremen, Germany — [2]Institute of Physics, Zagreb, Croatia — [3]University of Hamburg, Germany — [4]EPFL, Switzerland — [5]UCLouvain, Belgium

First-principles calculations of phonons are often based on the adiabatic approximation and a Brillouin-zone sampling that is not sufficient to capture Kohn anomalies. These shortcomings can be remedied through corrections to the phonon self-energy arising from the low-energy electrons. A well-founded correction method exists [Calandra, Profeta, and Mauri, Phys. Rev. B **82**, 165111 (2010)], which only relies on readily available (adiabatically) *screened* quantities. However, many-body theory suggests to use one *bare* electron–phonon vertex in the phonon self-energy [Giustino, Rev. Mod. Phys. **89**, 015003 (2017)] to avoid double counting. This can be seen as a limiting case of downfolding to *partially screened* phonons and interactions [Nomura and Arita, Phys. Rev. B **92**, 245108 (2015)]. We compare these approaches using the examples of $TaS_2$, $MgB_2$, n-doped $MoS_2$, and p-doped diamond. We confirm the robustness of the former method, while the latter allows for systematic improvements to describe correlations or metal–insulator transitions.

O 11.4  Mon 15:45  H6

**Implementation of DFT+U+J and the minimum-tracking linear response method for polaron formation modeling** — •Ziwei Chai[1,3], Karsten Reuter[3], Harald Oberhofer[1,2], and Limin Liu[4] — [1]Chair for Theoretical Chemistry, Technische Universität München — [2]Chair for Theoretical Physics VII, Universität Bayreuth, Germany — [3]Fritz-Haber-Institut der Max-Planck-Gesellschaft — [4]School of Physics, Beihang University

In many oxides charge carriers localize as small polarons. However, treating them with semi-local first-principles density-functional theory (DFT) tends to be a challenge usually addressed by hybrid DFT or Hubbard-corrected DFT+U. We present our implementation of DFT+U+J based on a "tensorial" representation of the subspace and the "minimum-tracking linear response method" which can determine U and J parameters from first-principles in the CP2K package. We performed systematic tests to prove the validity of the implementation.

Finally, the formation of polarons can be modeled by either breaking the symmetry of the initial structure or imposing an implicit or explicit constraining potential on the local orbital occupation. On top of our DFT+U+J implementation, we thus present the subspace occupancy-constraining potential (SOCP) approach to simulate the formation of polarons by constraining the occupancy number of the relevant local orbitals. Any polaronic configuration can thus straightforwardly be accessed without the need to explicitly break the system's symmetry.

O 11.5  Mon 16:00  H6

**Signatures of molecular conformation in the evolution of DFT-based single molecule conductance** — •Hector Vazquez — Inst. of Physics, Czech Academy of Sciences

Single molecules placed between two nanoelectrodes represent the ultimate limit in downscaling of electronic components. Electron transport simulations based on DFT-NEGF have enabled the understanding of conducting junctions and the interpretation of experiments [1]. However, these computationally costly calculations are often carried out for a small number of representative junction structures. In contrast, in room temperature experiments, the geometry of the molecule is expected to change significantly.

Here we describe and apply an approximate method to calculate molecular conductance within DFT for thousands of geometries. By combining it with room-temperature molecular dynamics (MD) simulations of the junction [2], we obtain the evolution of conductance for thousands of structure-conductance points. We analyze several geometric parameters and their effect on conductance, including quantum interference. This analysis on large datasets of DFT-based calculations reveals the signatures of molecular structure on junction conductance.
[1] F. Evers, R. Korytar, S. Tewari and J.M. van Ruitenbeek, Rev. Mod. Phys. 92, 35001 (2020)
[2] H. Vazquez, R. Skouta, S. Schneebeli, M. Kamenetska, R.Breslow, L. Venkataraman and M.S. Hybertsen, Nature Nanotechnol. 7, 663 (2012)

O 11.6  Mon 16:15  H6

**Spectral properties and thermodynamics of correlated metals via the algorithmic inversion of dynamical potentials** — •Tommaso Chiarotti[1], Andrea Ferretti[2], and Nicola Marzari[1] — [1]Theory and Simulations of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — [2]Centro S3, CNR–Istituto Nanoscienze, 41125 Modena, Italy

Dynamical potentials are needed to predict accurate spectral, transport, and in general embedding properties of materials. The nonlinearity introduced by the frequency changes at a fundamental level the problem to address, moving from the diagonalization of an operator, e.g., the Kohn and Sham Hamiltonian in density-functional theory, to the Dyson inversion of a self-energy. Here, we propose a novel treatment of frequency-dependence able to solve Dyson-like equations via an exact mapping to an effective non-interacting problem, extending to the non-homogeneous case the algorithmic inversion method (Chiarotti et al., PRR, 2022). A sum-over-poles representation for the self-energy, together with the static one-particle Hamiltonian, are used to build a (larger) effective Hamiltonian having the excitation energies of the system as eigenvalues and the Dyson orbitals as projections of the eigenvectors. As a case study, we consider the paradigmatic system of $S_rVO_3$ to compute accurate spectra and energetics of the material.