

HL 54: Frontiers in Electronic-Structure Theory - Focus on Electron-Phonon Interactions IV (joint session O/CPP/DS/HL)

Time: Wednesday 15:00–17:30

Location: GER 38

Invited Talk HL 54.1 Wed 15:00 GER 38

Electron-phonon interactions in realistic materials — ●FABIO CARUSO — Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Functional materials used in actual devices are typically doped, they operate at finite temperature, and they may be subject to perturbations such as, *e.g.*, external fields and light pulses. These aspects may alter profoundly the electron-phonon interaction (EPI), its influence on the electronic properties of solids, and even lead to the manifestation of novel emergent phenomena absent in perfect crystals.

We conducted a first-principles investigation of the EPI in functional materials at realistic operational conditions based on many-body perturbation theory. Our work reveals that: (i) *n*-type doping of polar oxides, such as EuO and TiO₂, allows one to trigger and control the formation of polarons (electrons dressed by a phonon cloud) [1]; (ii) in the record-breaking thermoelectric material SnSe, temperature may lead to a five-fold suppression of carrier lifetimes due to enhanced phonon emission [2]. Overall, the striking sensitivity to doping, temperature, and external fields, makes the EPI a powerful tool to tailor the optoelectronic properties of quantum materials. Possible strategies to extend the many-body theory of the EPI to the study of time-dependent phenomena will further be discussed [3].

[1] J. Riley, F. Caruso, C. Verdi, *et al.*, *Nature Commun.* **9** (1), 2305 (2018). [2] F. Caruso, M. Troppenz, S. Rigamonti, C. Draxl, *Phys. Rev. B* **99** (8), 081104 (2019). [3] F. Caruso, D. Novko, C. Draxl, arXiv:1909.06549v (2019).

HL 54.2 Wed 15:30 GER 38

Fully Anharmonic, Non-Perturbative First-Principles Theory of Electronic-Vibrational Coupling in Solids — MARIOS ZACHARIAS, MATTHIAS SCHEFFLER, and ●CHRISTIAN CARBOGNO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

The coupling between nuclear vibrations and the electronic structure plays a pivotal role for many material properties, including optical absorption and electronic transport. In this regard, however, today's state-of-the-art methodologies rely on two approximations [1]: the harmonic (phonon) approximation for the nuclear motion and the linear response description of the electronic structure with respect to harmonic displacements. In this work, we overcome **both** these approximations by performing fully anharmonic *ab initio* molecular dynamics (*aiMD*) calculations and by accounting for the non-perturbative, self-consistent response of the wave functions along the *aiMD* trajectory. By this means, we obtain fully anharmonic, vibronically renormalized spectral functions, from which macroscopic material properties like temperature-dependent band gaps and electronic transport coefficients are obtained. We validate our approach using silicon as an example, for which the traditional electron-phonon coupling formalism is recovered. Using cubic SrTiO₃ as example, we further demonstrate that anharmonic electronic-vibrational coupling effects are not captured in traditional formalisms, but they play a decisive role here and in other complex materials like perovskites.

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

HL 54.3 Wed 15:45 GER 38

Thermal conductivity of highly-doped Si: Role of electron-phonon and point-defect phonon scattering — ●BONNY DONGRE¹, JESÚS CARRETE¹, SHIHAI WEN², JINLONG MA², WU LI², NATALIO MINGO³, and GEORG KH MADSEN¹ — ¹Institute of Materials Chemistry, TU Wien, A-1060 Vienna, Austria. — ²Institute for Advanced Study, Shenzhen University, Shenzhen 518060, China — ³LITEN, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.

Theoretical investigation of the thermal conductivity reduction in highly-doped Si is an area of active research. Recently, first-principles electron-phonon scattering was found to produce a significant reduction in the thermal conductivity of highly-doped Si. However, the study could not reproduce the experimental results.

In the present work, we calculate the first-principles phonon scattering rates by electrons and point defects, and use them to calculate the thermal conductivity of highly-P- and B-doped Si for a range of temperatures and concentrations. We find that the phonon scatter-

ing by electrons dominates at carrier concentrations below 10¹⁹ cm⁻³ and is enough to reproduce the experimental thermal conductivity reduction at all temperatures. However, at higher defect concentrations point-defect phonon scattering contributes substantially to the thermal conductivity reduction even at room temperature. With a combined treatment of the phonon scattering by electrons as well as phonons, an excellent agreement is obtained with the experimental values at all temperatures.

HL 54.4 Wed 16:00 GER 38

Precise yet Fast High-Throughput Search for Thermal Insulators — ●FLORIAN KNOOP, THOMAS A.R. PURCELL, MATTHIAS SCHEFFLER, and CHRISTIAN CARBOGNO — Fritz-Haber-Institut der Max-Planck-Gesellschaft

We present a systematic and numerically precise computational search for thermal insulators in material space performed with the *FHI-vibes* high-throughput framework [1]. *FHI-vibes* employs a robust metric that quantifies the degree of anharmonicity in the nuclear dynamics via the statistical comparison of first-principles forces with those forces that would act in the harmonic approximation. This enables us to efficiently scan over many materials, including complex oxides and chalcogenides as well as ternary structures like perovskites. By this means, we single out strongly anharmonic systems, for which we perform *ab initio* Green-Kubo simulations to assess their thermal conductivities, thereby naturally including all anharmonic effects [2]. Our strategy allows to avoid redundant calculations and to achieve a much higher quality of information than traditional high-throughput studies. Besides validating the performed search and analyzing its results, we discuss how big-data analytics techniques can be utilized to further accelerate and guide this search.

[1] <https://vibes.fhi-berlin.mpg.de>

[2] C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017)

HL 54.5 Wed 16:15 GER 38

Ambivalent Impact of Electron-Phonon Interaction on Electronic and Transport Properties of Organic Semiconductors — ●FRANK ORTMANN — Center for Advancing Electronics Dresden, Technische Universität Dresden, Germany

Vibrations are omnipresent in molecules and of great importance in Organic Semiconductors due to the softness of the materials and the strong electron-phonon coupling. One possibility to investigate this interaction is to study the low-energy edge of optical absorption spectra, which lacks an in-depth understanding for organic materials. We have recently observed a strong dependence of low-energy excitonic features on the molecular building blocks in organic films, which we associated to molecular flexibility and polaron deformation. We will discuss implications of low-frequency molecular vibrations on the polaronic and excitonic density of states in donor-acceptor mixtures featuring charge-transfer excitons. We will also discuss how a distinguished treatment of strong-coupling molecular vibrations of different energies leads to an improved description of charge carrier transport in organic materials.

HL 54.6 Wed 16:30 GER 38

Quantum Nuclear Effects in Thermal Transport of Semiconductors and Insulators — ●HAGEN-HENRIK KOWALSKI¹, MARIANA ROSSI^{1,2}, MATTHIAS SCHEFFLER¹, and CHRISTIAN CARBOGNO¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²MPI for Structure and Dynamics of Matter, Hamburg, Germany

To date, the computation of thermal conductivities relies on either perturbation theory or (*ab initio*) molecular dynamics (MD) [1]. While perturbative approaches include quantum-nuclear effects (QNE), they typically neglect higher orders of anharmonicity. Conversely, classical MD includes all orders of anharmonicity, but neglects QNEs. To overcome these limitations, we have developed a formalism that accounts for **both** quantum-nuclear effects and all orders of anharmonicity. For this purpose, the nuclear dynamics are assessed via Thermostatted Ring Polymer MD (TRPMD) [2] and the thermal conductivity is obtained via the Green-Kubo formalism using a newly proposed TRPMD based heat-flux estimator. Using solid Argon and Silicon as model systems, we discuss the influence of QNEs on thermal transport by com-

paring velocity, energy, and heat-flux autocorrelation spectra. This allows to rationalize the impact of QNEs on vibrational frequencies, lifetimes, and on the thermal conductivity in different temperature regimes.

[1] C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901, (2017).

[2] M. Rossi, M. Ceriotti, D. Manolopoulos, *J. Chem. Phys.* **140**, 234116 (2014).

HL 54.7 Wed 16:45 GER 38

Speeding-up *ab initio* molecular dynamics with hybrid functionals using adaptively compressed exchange operator based multiple time stepping — ●SAGARMOY MANDAL and NISANTH N. NAIR — Department of Chemistry, Indian Institute of Technology Kanpur, India

Ab initio molecular dynamics (AIMD) with hybrid density functionals and a plane wave basis is known to predict the structural and dynamical properties of condensed matter systems accurately. However, such hybrid functional based AIMD simulations are not routinely used due to the high computational cost associated with the application of the Hartree-Fock exchange operator. We propose a strategy [1] to combine the Adaptively Compressed Exchange (ACE) operator formulation [2] and a multiple time step integration scheme to reduce the computational cost significantly. We also show that computing the ACE operator with localized orbitals can further improve the computational efficiency. Finally, we use this method in combination with the Well-Sliced Metadynamics approach to compute the free energy barrier of chemical reactions in systems containing hundreds of atoms.

[1] S. Mandal, N.N. Nair, *J. Chem. Phys.* **151** (2019) 151102.

[2] Lin Lin, *J. Chem. Theory Comput.* **12** (2016) 2242.

HL 54.8 Wed 17:00 GER 38

Calculation of current-induced heating and vibrational instabilities in single molecule circuits — GIUSEPPE FOTI and ●HECTOR VAZQUEZ — Inst. of Physics, Academy of Sciences of the Czech Rep., CZ

Current-induced heating in molecular wires arises from the interaction between tunneling electrons and localized vibrations. Vibrational instabilities occur when excitation of molecular vibrations is not balanced by dissipation mechanisms, and can lead to the breakdown of the junction. In this talk I will address predictions for vibrational instabili-

ties in single molecule junctions with separated unoccupied resonances. We use DFT-NEGF to study the electronic structure of the junction under an applied bias, while rates of absorption and emission of vibrations are calculated using kinetic equations [1,2]. We find and characterize several unstable modes. These results are then generalized using model calculations to generate a stability diagram of the junction under bias [3]. The talk will discuss the effect of a self-consistent treatment of electron-vibration interaction, and highlight the role played by the structure of the electron-vibration coupling matrix. Our work reveals the interplay of electronic structure and electron-vibration coupling in a broad class of molecular wires.

[1] J-T Lü, P. Hedegaard and M. Brandbyge, *Phys. Rev. Lett.* **107**, 046801 (2011).

[2] G. Foti and H. Vázquez, *J. Phys. Chem. C* **121**, 1082 (2017).

[3] G. Foti and H. Vázquez, *J. Phys. Chem. Lett.* **9**, 2791 (2018).

HL 54.9 Wed 17:15 GER 38

***Ab Initio* Green-Kubo Approach of Charge Transport in Crystalline Solids** — ●ZHEN-KUN YUAN, MARIOS ZACHARIAS, MATTHIAS SCHEFFLER, and CHRISTIAN CARBOGNO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

State-of-the-art approaches for calculating the charge transport coefficients in crystalline materials rely on a harmonic description of the lattice vibrations and a perturbative treatment of electron-phonon couplings (EPCs) [1]. For materials featuring sizable anharmonic lattice vibrations and/or strong EPCs, such approaches are, however, not applicable. Here, we present an *ab initio* approach based on the Green-Kubo theory of linear response [2] that does neither rely on the harmonic approximation nor on a perturbative treatment of EPCs, thus overcoming these issues. The electrical conductivity is obtained from the time correlations of the electric charge flux, which is computed along fully anharmonic *ab initio* molecular dynamics trajectories. We demonstrate our approach by calculating the electrical conductivity of the harmonic material Si and the anharmonic SrTiO₃. We carefully check the convergence behavior of the calculated results with respect to supercell size and examine possible strategies to overcome finite-size effects [3].

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

[2] R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Jpn.* **12**, 1203 (1957).

[3] C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).