CPP 75: 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   CPP 75.1   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 perturba-
tions 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 per-
turbation theory. Our work reveals that: (i) n-type doping of polar
oxides, such as EuO and TiO_2, allows one to trigger and control the for-
mation 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 opto-
electronic properties of quantum materials. Possible strategies to ex-
tend 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).

CPP 75.2   Wed 15:30   GER 38
**Fully Anharmonic, Non-Perturbative First-Principles The-
ory 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 har-
monic (phonon) approximation for the nuclear motion and the linear
response description of the electronic structure with respect to har-
monic displacements. In this work, we overcome **both** these approx-
imations by performing fully anharmonic *ab initio* molecular dynam-
ics (*ai*MD) calculations and by accounting for the non-perturbative,
self-consistent response of the wave functions along the *ai*MD trajec-
tory. By this means, we obtain fully anharmonic, vibronically renor-
malized spectral functions, from which macroscopic material proper-
ties 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 $SrTiO_3$ as example, we further demonstrate
that anharmonic electronic-vibrational coupling effects are not cap-
tured 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).

CPP 75.3   Wed 15:45   GER 38
**Thermal conductivity of highly-doped Si: Role of electron-
phonon and point-defect phonon scattering** — •Bonny
Dongre[1], Jesús Carrete[1], Shihao Wen[2], Jinlong Ma[2], Wu Li[2],
Natalio Mingo[3], and Georg KH Madsen[1] — [1]Institute of Ma-
terials Chemistry, TU Wien, A-1060 Vienna, Austria. — [2]Institute
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[3]LITEN, 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 reduc-
tion 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 scat-
tering 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 10^{19} cm^{-3}
and is enough to reproduce the experimental thermal conductivity re-
duction 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.

CPP 75.4   Wed 16:00   GER 38
**Precise yet Fast High-Throughput Search for Thermal In-
sulators** — •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 dynam-
ics 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 con-
ductivities, 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-thoughput 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)

CPP 75.5   Wed 16:15   GER 38
**Ambivalent Impact of Electron-Phonon Interaction on Elec-
tronic 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 in-
teraction 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 im-
plications 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.

CPP 75.6   Wed 16:30   GER 38
**Quantum Nuclear Effects in Thermal Transport of Semicon-
ductors and Insulators** — •Hagen-Henrik Kowalski[1], Mariana
Rossi[1,2], Matthias Scheffler[1], and Christian Carbogno[1] —
[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany
— [2]MPI for Structure and Dynamics of Matter, Hamburg, Germany

To date, the computation of thermal conductivities relies on either per-
turbation 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 over-
come 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 ob-
tained via the Green-Kubo formalism using a newly proposed TRPMD
based heat-flux estimator. Using solid Argon and Silicon as model sys-
tems, 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).

CPP 75.7   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.

CPP 75.8   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 instabilities 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).

CPP 75.9   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 $SrTiO_3$. 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).