DS 23: Frontiers in Electronic-Structure Theory - Focus on Electron-Phonon Interactions III (joint session O/HL/CPP/DS)

Time: Wednesday 10:30–13:30   Location: GER 38

Invited Talk   DS 23.1   Wed 10:30   GER 38
Hybrid Perovskites: polarons, excitons and phase diagrams
— •Georg Kresse, Menno Bokdam, and Ryosuke Jinnouchi —
University of Vienna, Faculty of Physics and Center for Computational
Materials Sciences

Halide perovskites are very promising solar cell materials. The first
part of this presentation studies the formation of polarons and exci-
tons in MAPbI3. We show that both, polarons and excitons, possess
about similar binding energies. To obtain accurate results, the cal-
culations have to be carefully converged with respect to the k-point
sampling, something that has been often "overlooked" in the past [1].

The second part of the talk presents studies on the finite temper-
ature behavior of MAPbI3. To achieve the required long simulation
time and large length scales, an on-the-fly machine learning scheme
that generates force fields automatically during first principles molec-
ular dynamics simulations is used. This force field opens up the re-
quired time and length scales, while retaining the distinctive chemical
precision of first principles methods [2]. Using machine learned poten-
tials, isothermal-isobaric simulations give direct insight into the un-
derlying microscopic mechanisms of the phase transitions. We observe
that MAPbI3 is an very dynamic material even at room temperature,
putting some question marks on the hereto considered static models.

[1] M. Bokdam, T. Sander, A. Stroppa, S. Picozzi, D. D. Sarma, C.
Franchini, G. Kresse, Scientific Rep. 6, 28618 (2016); [2] R. Jinnouchi,
J. Lahnsteiner, F. Karsai, G. Kresse, M. Bokdam, PRL 122, 225701
(2019).

DS 23.2   Wed 11:00   GER 38
**Assessing ab-initio methodology to compute electronic prop-
erties of organic-inorganic metal halide perovskites** —
•Cecilia Vona, Dmitrii Nabok, and Claudia Draxl — Institut für
Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin,
Germany

Organic-inorganic metal halide perovskites (HaPs) are materials
widely studied for their light-harvesting properties. Owing to the
interplay between strong electron-electron interaction and spin-orbit
coupling, their theoretical investigation is still a challenge. Here we
evaluate the methodology to compute their electronic structure. To
this extent, we explore several approaches, within density-functional
theory and many body perturbation theory, to compute the electronic
structure of PbI$_2$, which is the precursor of many HaPs. Spin-orbit
coupling effects are taken into account, and the hybrid functionals
PBE0 and HSE are at the center of the investigation. We first explore
several methods to determine the mixing parameter α, which in PBE0
and HSE defines the amount of Hartree-Fock exchange mixed with
the semi-local functional PBE. We then use the results obtained from
HSE and PBE0 for different values of α as starting point of G_0W_0
calculations. All the calculations are performed with the full-potential
all-electron computer package exciting, in which LAPW+lo bases are
implemented. We observed that hybrid functionals with a proper α
value are most suitable to compute the electronic structure of PbI$_2$.
Moreover, we show that the methodology is transferable to CsPbI$_3$,
and we expect the same behavior for the lead-iodine perovskites.

DS 23.3   Wed 11:15   GER 38
**Rashba-Dresselhaus Effect in Two Dimensional Layered
Halide Perovskites** — •Benedikt Maurer[1,2], Claudia Draxl[1,2],
and Christian Vorwerk[1,2] — [1]Institut für Physik and IRIS Adler-
shof, Humboldt-Universität zu Berlin, 12489 Berlin — [2]European The-
oretical Spectroscopy Facility

It has been shown that huge spin-orbit coupling in bulk hybride organic
inorganic perovskites in combination with broken inversion symmetry
leads to Rashba-Dresselhaus splitting, which influences the optoelec-
tronic properties. This indicates that such effects also affect the opto-
electronic properties of their two dimensional layered relatives, which
are promising candidates as new light emitting materials. In this work,
we aim at understanding which inversion symmetry breaking can lead
to the Rashba-Dresselhaus effect in those materials. For this purpose,
we develop model structures, where we replace the organic compounds
by Cs atoms and disregard possible distortions in the inorganic lay-
ers, resulting in the structural composition Cs$_{n+1}$Pb$_n$I$_{3n+1}$. Using

the all-electron full-potential density-functional-theory code exciting,
we systematically study how atomic distortions impact the band struc-
ture for n=1, 2 and ∞. We identify displacement patterns that yield
Rashba-Dresselhaus splitting, and determine the size of the splitting
as a function of the displacement. Furthermore, we analyze the spin
textures in electronic states around the band gap to differentiate be-
tween Rashba and Dresselhaus effect. Our study reveals in-plane lead
displacements as the origin of the Rashba-Dresselhaus splitting.

DS 23.4   Wed 11:30   GER 38
Intrinsic polarons on polar surfaces — •Michele Reticcioli[1,2],
Zhichang Wang[2], Igor Sokolovic[2], Michael Schmid[2], Ul-
rike Diebold[2], Martin Setvin[2], and Cesare Franchini[2,3] —
[1]University of Vienna, Center for Computational Materials Science,
Vienna, Austria — [2]Institute of Applied Physics, Technische Univer-
sitaet Wien, Vienna, Austria — [3]University of Bologna, Department
of Physics and Astronomy, Bologna, Italy

Uncompensated charge at the surface boundary of polar materials
is conventionally expected to form a two dimensional electron gas
(2DEG), as a result of the alternating charged-plane stacking in the
ionic crystals, interrupted by the surface cut. By means of density-
functional theory calculations and surface-sensitive experiments, we
propose a different paradigm able to accommodate the uncompen-
sated charge in a more effective way, establishing a more favorable
ground state for the system, that is the polaron formation (local lat-
tice distortions coupled with charge localization). In fact, the intrinsic
uncompensated charge tends to spontaneously localize and form po-
larons, rather than a 2DEG. Only beyond the critical polaron density,
excess charge arising from external doping or defects starts to build
dispersed electronic states. Here, we show how polarons and 2DEG
compete on the polar KTaO3(001) surface.

DS 23.5   Wed 11:45   GER 38
**Polarons in extended p-conjugated systems: the role of elec-
tron correlation.** — •Daniele Fazzi[1], Klaus Meerholz[1], and
Fabrizia Negri[2] — [1]Institut für Physikalische Chemie, Universität zu
Köln, Luxemburger str. 116, 50939 Köln, Germany — [2]Dipartimento
di Chimica, Università di Bologna, via F. Selmi, 2, 40126 Bologna,
Italy

Polarons play a crucial role in governing charge transfer in organic
materials. An accurate description of their electronic structure and
electron-phonon couplings is mandatory to understand their response
and transport properties.

We report a comprehensive investigation of polarons in extended
p-conjugated systems (ladder-type polymers, graphene nano-ribbons,
and cyanine-based compounds [1-2]). We show how spin polarized
DFT lead to solutions of the polarons wavefunction which are not the
most stable ones. This aspect, can be traced back to the multirefer-
ence character of polarons. Broken symmetry DFT can address the
electronic and structural properties of polarons, providing a correct
assessment of charge transport parameters, otherwise incorrectly com-
puted [3]. Multi-reference wavefunction methods are also considered
to take into account correlation effects in charged and excited states.

Our study calls for a careful assessment in the description of
charged/excited states in conjugated materials.

[1] Wang, S., et al., Adv. Mater. 2018, 30, 1801898. [2] Medina, S.
et al., Phys. Chem. Chem. Phys., 2019, 21, 7281-7288. [3] Fazzi, D.
et al, J. Mat. Chem. C., 2019, 7, 12876-12885.

DS 23.6   Wed 12:00   GER 38
**Optical and x-ray absorption spectra of MgO from first-
principles including many-body effects** — •Vijaya Begum,
Markus E Gruner, and Rossitza Pentcheva — Faculty of Physics
and Centre for Nanointegration (CENIDE), University of Duisburg-
Essen, Duisburg, Germany

We discuss the optical and x-ray absorption (XAS) spectra of MgO − a
wide band gap oxide with versatile applications − in the framework of
density functional theory (DFT) including many-body and excitonic
corrections. The quasi-particle band gap improves over DFT with
PBEsol as the starting exchange-correlation functional (4.58 → 7.52
eV) and is overcorrected with the hybrid functional HSE06 (6.58 →

8.53 eV) when compared to experiment (7.7 eV). Including excitonic effects by solving the Bethe-Salpeter equation (BSE) leads to excellent agreement with the experimental spectrum both for the real and imaginary part of the dielectric function, when starting with the HSE06 functional. Furthermore, the x-ray absorption spectra of the O and Mg K-edge calculated with the Exciting code exhibit good agreement with experiment regarding the positions of the prominent peaks, underlining the importance of including the core-hole and electron interactions within the G_0W_0+BSE. Projection of the electron-hole coupling coefficients from the BSE eigenvectors on the band structure allows to explore the origin of the peaks and identify the orbital character of the relevant contributions.

DS 23.7   Wed 12:15   GER 38

Strain effects on the lattice-dynamical properties of titanium dioxide — •Peter Weber, Sebastian Tillack, Pasquale Pavone, and Claudia Draxl — Humboldt-Univeristät zu Berlin, Physics Department and IRIS Adlershof, Germany

A fingerprint of temperature-related anharmonic effects in a crystal is the change of the phonon frequencies with the volume. For anisotropic crystals, this variation must be generalized by the introduction of the mode Grüneisen tensor, which expresses the change of the phonon frequencies with respect to any applied strain. In this work, we present the results of an *ab-initio* investigation of the strain effects on the lattice-dynamical properties of the rutile and anatase phases of TiO_2. In particular, we focus our attention to the determination of the generalized Grüneisen parameters at the Brillouin zone center. In order to obtain all independent components of the Grüneisen tensor for these phases, all polar and nonpolar phonon frequencies at the Γ point are calculated for several strained configurations. These calculations are performed using density-functional theory as implemented in the full-potential all-electron software package `exciting` [1]. The connection between the Grüneisen tensors of the acoustic branches and the elastic constants of these materials is analyzed and discussed. Our results are also compared with available Raman scattering data for strained TiO_2.

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

DS 23.8   Wed 12:30   GER 38

Ab-initio phonon self-energies and fluctuation diagnostics of phonon anomalies: lattice instabilities from Dirac pseudospin physics in transition-metal dichalcogenides — •Jan Berges[1], Erik van Loon[1], Arne Schobert[1], Malte Rösner[2], and Tim Wehling[1] — [1]Institute for Theoretical Physics and Bremen Center for Computational Materials Science, University of Bremen, Germany — [2]Institute for Molecules and Materials, Radboud University Nijmegen, The Netherlands

We present an ab-initio approach for the calculation of phonon self-energies and their fluctuation diagnostics, which allows us to identify the electronic processes behind phonon anomalies. Application to the prototypical transition-metal dichalcogenide 1H-TaS_2 reveals that coupling between the longitudinal–acoustic phonons and the electrons from an isolated low-energy metallic band is entirely responsible for phonon anomalies like mode softening and associated charge-density waves observed in this material. Our analysis allows to distinguish between different mode-softening mechanisms including matrix-element effects, Fermi-surface nesting, and Van Hove scenarios. We find that matrix-element effects originating from a peculiar type of Dirac pseudospin textures control the charge-density-wave physics in 1H-TaS_2 and similar transition-metal dichalcogenides.

DS 23.9   Wed 12:45   GER 38

Toward a general non-local polarizability density functional for van der Waals dispersion interactions — •Szabolcs Góger, Dmitry Fedorov, Péter Szabó, and Alexandre Tkatchenko — University of Luxembourg, 1511 Luxembourg, Luxembourg

Density functional theory (DFT), while being a workhorse for electronic structure calculations, struggles with describing long-range electron correlations including van der Waals (vdW) dispersion interactions. Various promising approaches have been developed to include vdW interactions in DFT, but a broadly applicable method is yet to be found [1,2]. The first key issue is developing a general density functional for non-local polarizability in molecules and solids. In this work, we use different known properties of atomic and molecular polarizabilites including the direct relation between the dipole polarizability and vdW radius unveiled recently [3]. Diverse methods starting with the Slater-Kirkwood approach [4] are applied to simple quantum mechanical systems like the Drude oscillator and the hydrogen atom under the effect of various electric fields. Our model studies along with prior work on semi-local polarizability functionals [5] pave the way toward developing a unified non-local polarizability functional for molecules and materials.

[1] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
[2] Stöhr *et al.*, Chem. Soc. Rev. **48**, 4118 (2019)
[3] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)
[4] Slater and Kirkwood, Phys. Rev. **37**, 682 (1931)
[5] Vydrov and Van Voorhis, Phys. Rev. Lett. **103**, 063004 (2009)

DS 23.10   Wed 13:00   GER 38

Insights into van der Waals interactions from the quantum Drude oscillator model — •Dmitry Fedorov, Martin Stöhr, and Alexandre Tkatchenko — University of Luxembourg, 1511 Luxembourg, Luxembourg

The quantum Drude oscillator (QDO) model [1] represents the response of all valence electrons in an atom by a single Drude particle with its charge, mass, and characteristic frequency. Due to the simple form, this model serves as an insightful approach for the description of atomic response properties and van der Waals (vdW) interactions [2]. Recently, the QDO model helped to unveil a non-trivial relation between the dipole polarizability and the atomic volume, $\alpha_{\mathrm{dip}} \propto V^{4/3}$, [3] as well as the surprising direct relation between the multipole polarizabilities and the equilibrium distances in vdW-bonded atomic dimers [4]. Here, we provide a detailed insight into the physical background of the aforementioned findings. The connection between different striking scaling laws obtained by diverse ways shows the inner consistency and power of this simple but efficient model. We discuss the importance of the revealed quantum-mechanical relations between response and geometric properties of atoms for computational models like the Tkatchenko-Scheffler [5] and the many-body dispersion [2] methods.

[1] Jones *et al.*, Phys. Rev. B **87**, 144103 (2013)
[2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
[3] Kleshchonok and Tkatchenko, Nat. Commun. **9**, 3017 (2018)
[4] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)
[5] Tkatchenko and Scheffler, Phys. Rev. Lett. **102**, 073005 (2009)

DS 23.11   Wed 13:15   GER 38

Conical intersections in molecular systems: 3D vs 2D models — •Erik Pillon, Dmitry Fedorov, Péter Szabó, and Alexandre Tkatchenko — University of Luxembourg, 1511 Luxembourg

The molecular Aharonov-Bohm effect [1], covering various phenomena caused by the Berry (geometric or topological) phase in molecular systems, is an important playground for understanding fundamental quantum physics as well as for building quantum electronic devices. The related non-adiabatic effects, stemming from the coupling between the electron and nuclear degrees of freedom, are especially pronounced in systems possessing conical intersections (CI) in potential energy surfaces, ubiquitous in condensed matter and molecular physics. Many toy models have been introduced to study the influence of CIs on the nuclear dynamics from a general point of view. However, most of them, including the linear vibronic coupling model [2, 3] widely used in literature, employ two-dimensional (2D) real Hamiltonians. In our work, we check whether such models capture all the important features of real molecular systems. To this end, we perform a comparison of the conventional approaches with the general treatment of a CI within the three-dimensional (3D) complex Hamiltonian possessing SU(2) symmetry [4]. The features present within the 3D model but missing in the 2D case are identified and discussed.

[1] Zygelman, J. Phys. B: At. Mol. Opt. Phys. **50**, 025102 (2017)
[2] Longuet-Higgins *et al.*, Proc. R. Soc. A **244**, 1 (1958)
[3] Jahn and Teller, Proc. R. Soc. A **161**, 220 (1937)
[4] Berry, Proc. R. Soc. A **392**, 45 (1984)