CPP 15: Frontiers in Electronic-Structure Theory - Focus on Electron-Phonon Interactions I (joint session O/HL/CPP/DS)

Electronic-structure calculations from first principles have become an indispensable and ubiquitous tool in materials modeling, design, and discovery. One of the outstanding challenges in this area is to study materials at finite temperature, in order to achieve a more realistic description of materials properties and to enable direct comparison with experimental data. To address this challenge it will be necessary to move beyond the static-ions approximation, and to devise systematic approaches for incorporating the effects of electron-phonon coupling, phonon-phonon interactions, and phonon-assisted quantum processes in state-of-the-art electronic-structure methods. The invited lectures will cover recent progress in the broad area of electron-phonon physics from the point of view of first-principles calculations. More generally, the symposium will also cover other areas of first-principles computational materials science (basic methods and applications).

Claudia Draxl (Humboldt-Universität zu Berlin, Germany), Feliciano Giustino (University of Texas at Austin, USA), Matthias Scheffler (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

Time: Monday 10:30–12:45   Location: GER 38

Invited Talk   CPP 15.1   Mon 10:30   GER 38
Predominance of non-adiabatic effects in zero-point renormalization of electronic energies. — •Xavier Gonze[1,2], Anna Miglio[1], Véronique Brousseau-Couture[3], Gabriel Antonius[4,5], Yang-Hao Chan[4], Steven Louie[4], Giantomassi Matteo[1], and Michel Côté[3] — [1]UCLouvain, Belgium. — [2]Skoltech, Moscow, Russia. — [3]Dept. Physique, U. Montréal, Canada. — [4]Dept. Physics, U. California Berkeley & Materials Sci. Div. NBNL Berkeley, CA, USA. — [5]Dept. Chim., Bio. & Physique, U. Québec Trois-Rivières, Canada.

Electron-phonon interaction induces variation of bandgaps with temperature, and zero-point motion renormalization (ZPR) even at 0K. Ignored in most calculations, ZPR has been evaluated recently for several materials, often relying on the adiabatic approximation, reasonably valid for materials without infrared (IR) activity, but eagerly applied to other materials. We present the first large-scale (29 materials) first-principles evaluation of ZPR beyond the adiabatic approximation [1]. For materials with light elements the ZPR is often larger than 0.3 and up to 1.1 eV: it is useless to go beyond G0W0 without including ZPR in such materials. For IR-active materials, global agreement with experimental data is obtained only with nonadiabatic effects. They even dominate ZPR for many materials. A generalized Fröhlich model that represents accurately nonadiabatic effects accounts for more than half the ZPR for a large set of materials.
[1] A. Miglio, V. Brousseau-Couture, G. Antonius, Y.-H. Chan, S.G. Louie, M. Giantomassi, M. Côté, and X. Gonze. Submitted.

CPP 15.2   Mon 11:00   GER 38
A generalized first-principles formalism for the electron-phonon renormalization of electronic energy eigenvalues — •Jae-Mo Lihm[1,2,3] and Cheol-Hwan Park[1,2,3] — [1]Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea — [2]Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Korea — [3]Center for Theoretical Physics, Seoul National University, Seoul 08826, Korea

The interaction between electrons and phonons induce a temperature-dependent renormalization of electronic energy eigenvalues [1]. The perturbative theory of Allen, Heine, and Cardona (AHC) [2] enables an efficient first-principles calculation of the renormalized electronic eigenenergies. The temperature dependence of the electronic bandgap, optical responses, and topological properties of real materials have been investigated within the AHC formalism. In this study, we generalize the AHC formalism [3] so that it could be applied to a broader class of materials. We demonstrate our formalism by calculating the temperature-dependent electronic energy eigenvalues of representative materials.
[1] F. Giustino, Rev. Mod. Phys. 89, 015003 (2017)
[2] P. B. Allen and V. Heine, J. Phys. C 9, 2305 (1976); P. B. Allen and M. Cardona, Phys. Rev. B 24, 7479 (1981); 27, 4760 (1983).
[3] J.-M. Lihm and C.-H. Park, unpublished.

CPP 15.3   Mon 11:15   GER 38
Electron-phonon interactions beyond the Born-Oppenheimer approximation in Kohn Sham theory — •Nikitas Gidopoulos — Department of Physics, Durham University, South Road, Durham, DH1 3LE, U.K.

I shall present our work on non-adiabatic corrections to the electron-phonon matrix elements, in density functional theory beyond the Born Oppenheimer approximation, where the Kohn-Sham single-particle potential contains a non-adiabatic correction term [1]. This term depends self-consistently on the nuclear vibrational wave function. The standard expansion of the non-adiabatic KS potential around the nuclear equilibrium positions yields electron-phonon matrix elements beyond the BO approximation.
[1] NI Gidopoulos, EKU Gross, Phil. Trans. R. Soc. A 372, 20130059 (2014). http://dx.doi.org/10.1098/rsta.2013.0059

CPP 15.4   Mon 11:30   GER 38
Renormalized second-order perturbation theory for the band gap and single-particle excitations of solids — •Maria Dragoumi[1], Sergey V. Levchenko[2,1], Igor Ying Zhang[3,1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]Skolkovo Institute of Science and Technology, Moscow, RU — [3]Fudan University, Shanghai, CN

We report an efficient implementation of renormalized second-order single-particle energies for periodic systems in an all-electron numeric atomic orbital framework. Starting from second-order perturbation theory, which is single-electron self-interaction free as a virtue of the first-order and second-order exchange diagrams, we use the Dyson equation to sum up infinite number of diagrams [1,2]. In our implementation we use Ewald summation for the long-range part of the Coulomb interaction. This results in an integrable singularity in k-space, which has to be carefully evaluated in order to ensure proper convergence with k-point mesh density. For this purpose we develop an approach based on a generalization of the Gygi-Baldereschi method. The dependence on the starting point of the perturbation theory is examined. The new approach shows a competitive or even superior performance for the description of band-energies compared to the current state-of-the-art methods such as hybrid functionals and G^0W^0 approximation. Thus, with a good starting point this method becomes a powerful tool for the prediction of band energies for a variety of materials.
[1] J. Sun and R. J. Bartlett, J. Chem. Phys. 104, 8553 (1996).
[2] A. Grüneis et al., J. Chem. Phys. 133, 074107 (2010).

CPP 15.5   Mon 11:45   GER 38
Band structure of semiconductors and insulators from Koopmans-compliant functionals — •Riccardo De Gennaro[1], Nicola Colonna[2], and Nicola Marzari[1] — [1]Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — [2]Laboratory for Neutron Scattering and Imaging (LNS), Paul Scherrer Institute, 5232 Villigen, Switzerland

Koopmans-compliant functionals provide a novel orbital-density-dependent framework for an accurate evaluation of spectral properties, obtained imposing a generalized piecewise-linearity condition on the total energy of the system with respect to the occupation of each orbital. In crystalline materials, due to the orbital-density-dependent nature of the functionals, minimization of the total energy leads to a ground-state set of variational orbitals that are localized and break

the periodicity of the underlying lattice. Despite that, thanks to the Wannier-like character of the variational orbitals, we show that the Bloch symmetry is still preserved and it is possible to describe the electronic energies through a band structure picture. In this talk I will present results for some benchmark semiconductors and insulators, obtained by unfolding the electronic bands obtained with Gamma-point-only calculations.

CPP 15.6 Mon 12:00 GER 38

Dynamical vertex corrections beyond GW from time-dependent density-functional theory — •Georg S. Michelitsch[1,2], Lucia Reining[1,2], and Matteo Gatti[1,2] — [1]Laboratoire des Solides Irradiés, École Polytechnique, F-91128 Palaiseau, France — [2]European Theoretical Spectroscopy Facility (ETSF)

Strong many-body effects in solid state materials are the reason for features such as satellites in electronic excitation spectra. Many-body perturbation theory approaches based on the Green's function formalism are the state-of-the-art in their understanding, commonly applied in terms of the GW approximation to the self-energy, which neglects the so-called vertex correction in Hedin's equations. Although successful for some observables such as band gaps, this approximation cannot sufficiently well describe satellite peaks observed in experiment. Vertex corrections beyond GW can be taken into account thanks to time-dependent density-functional theory[1]. However, only adiabatic approximations have been considered so far. Here we make use of a non-adiabatic approximation[2] to investigate dynamical vertex corrections within a model self-energy. We compare our results to calculations where a static vertex is included and report first successes in terms of a correction to the satellites in the spectral function of sodium.

[1] R. Del Sole et al. *Phys. Rev. B*, 49, 8024 (1994)
[2] M. Panholzer et al. *Phys. Rev. Lett.*, 120, 166402 (2018)

CPP 15.7 Mon 12:15 GER 38

Large-scale benchmark of exchange-correlation functionals for the determination of electronic band gaps of solids — •Pedro Borlido[1], Thorsten Aull[2], Ahmad Huran[2], Fabien Tran[3], Miguel Marques[2], and Silvana Botti[1] — [1]Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany — [2]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany —

[3]Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

We compile a large dataset designed for the efficient benchmarking of exchange-correlation functionals for the calculation of electronic band gaps.The dataset comprises information on the experimental structures and band gaps of 472 non-magnetic materials, and includes a diverse group of covalent-, ionic-, and van der Waals-bonded solids.

We used it to benchmark a set of 30 functionals sampling the entirety of Jacob's Ladder. This includes well established functionals such as PBE, mBJ and HSE06, as well as several other less known functionals.

The comparison of experimental and theoretical band gaps shows that mBJ is at the moment the best available density functional, closely followed by HSE06. Other functionals such as HLE16, HLE17, AK13 and TASK also show overall good performance.

CPP 15.8 Mon 12:30 GER 38

Assessment of Approximate Methods for Anharmonic Free Energies — •Venkat Kapil[1], Edgar Engel[2], Mariana Rossi[3], and Michele Ceriotti[1] — [1]Swiss Federal Institute of Technology, Switzerland — [2]Department of Physics, University of Cambridge, UK — [3]MPI for Structure and Dynamics of Matter, Hamburg, Germany

Quantitative estimations of thermodynamic stabilities, measured by free energies, must take into account thermal and quantum zero-point nuclear motion. While these effects are easily estimated within a harmonic approximation, corrections arising from the anharmonic nature of the interatomic potential are often crucial and their accurate computations require expensive path integral simulations. Consequently, different approximate methods for computing affordable estimates of anharmonic free energies have been developed. Understanding which of the approximations involved are justified for a given system is complicated by the lack of comparative benchmarks. We here assess the accuracy of some of the commonly used approximate methods: vibrational self-consistent field and self-consistent phonons by comparing anharmonic corrections to Helmholtz free energies against reference path integral calculations. We study a diverse set of systems, ranging from simple weakly anharmonic solids to flexible molecular crystals with freely-rotating units and conclude that efforts towards obtaining computationally-feasible anharmonic free-energies of molecular systems must focus at reducing the expense of path integral methods. *Kapil, Venkat, et al. Assessment of Approximate Methods for Anharmonic Free Energies. JCTC, 2019, doi:10.1021/acs.jctc.9b00596.*