Generalization of the Fröhlich model to first principle calculations: dynamical effects in zero-point renormalization.

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Computing the zero-point renormalization (ZPR) of the electronic bandgap due to electron-phonon coupling from first principles is a computationaly challenging task, especially for polar materials, for which a very fine phonon wavevector sampling is required [1, 2]. By contrast, the well-known Fröhlich Hamiltonian gives in the perturbative regime a simple analytical formula for the polaron binding energy, based on a few parameters that can be obtained from experiments or from first-principles calculations.

We present the first large-scale (29 materials) first-principles evaluation of the zero-point renormalization of band edges beyond the adiabatic approximation, and obtain an unprecedenced agreement with experiment for both the stabilization energy due to electron-phonon coupling and the final band gap. For infrared-active materials, global agreement with available experimental data is obtained only when dynamical effects are taken into account : they even dominate zero-point renormalization for many materials.

We also present a generalized Fröhlich model that represents accurately the dynamical contributions, and assess its accuracy against first-principles results. This model captures the full complexity of real materials, allowing for multiple phonon branches as well as anosotropic and degenerate band extrema. It describes the essential physics and accounts for more than half of the total ZPR for a large set of materials, especially for the valence band edges, despite its neglect of interband electronic transitions, Debye-Waller contribution and acoustic phonon contributions present in the full first-principles approach. By the same token, the domain of validity of the hypotheses underlying the Fröhlich model, used for decades, is established. We finally use this model to develop a method to estimate the converged ZPR from coarser phonon samplings.

References

[1] G. Antonius et al, Phys. Rev. B **92**, 085137 (2015).

[2] S. Poncé et al, J. Chem. Phys. **143**, 102813 (2015).