DFT-based thermal properties: three levels of error management

It is often computationally expensive to predict finite-temperature properties of a crystal from density-functional theory (DFT). The temperature-dependent thermal expansion coefficient α, for example, is calculated from the phonon spectrum, and the melting temperature T_m can only be obtained from *ab initio* molecular dynamics. Alternatively, semi-empirical relations already provide good estimates at a significantly lower computational cost. These relations link complex quantities, such as α and T_m, to much simpler DFT predictors, such as the cohesive energy or the bulk modulus. The difference between these semi-empirical estimates and experiment is governed by three sources of errors: the numerical accuracy of the DFT implementation [1,2], the limitations of the exchange-correlation functional [1], and the approximations involved in the semi-empirical relation itself [3]. We quantify each of these errors, and find them to contribute according to the order of listing: least for the implementation dependence and most for the effect of the semi-empirical relation. Despite these deviations, some semi-empirical relations do outperform more fundamental methods. An estimate for the Grüneisen parameter that is based on the pressure derivative of the bulk modulus, for example, yields better predictions for the thermal expansion coefficient at room temperature than quasiharmonic phonon theory [3].

[1] K. Lejaeghere, V. Van Speybroeck, G. Van Oost, and S. Cottenier, ' Error Estimates for Solid-State Density-Functional Theory Predictions: An Overview by Means of the Ground-State Elemental Crystals', *Crit. Rev. Solid State* **39**, 1-24 (2014). [open access at DOI: 10.1080/10408436.2013.772503]
[2] https://molmod.ugent.be/DeltaCodesDFT.
[3] K. Lejaeghere, J. Jaeken, V. Van Speybroeck, and S. Cottenier, '*Ab-initio*-based thermal property predictions at a low cost: an error analysis', submitted to *Phys. Rev. B*.