The ground state elemental crystals as a guideline for the assessment of solid state DFT accuracy

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Abstract

A central issue when applying DFT for property predictions is an assessment of the error bars on the computed quantities. These are usually determined by performing calculations for a set of experimentally well-known benchmark systems. For molecules, some commonly accepted test sets are available for the evaluation of various properties at various levels of theory. Similar systematic and broad tests for crystalline solids are not that easily found. Therefore, several basic properties have been computed for a test set with nearly all ground state elemental crystals. This test set contains many different elements, crystal structures and chemical bond types in a natural way. Three general-purpose DFT codes have been employed, using a Perdew-Burke-Ernzerhof functional. The following examples summarize a comparison between VASP [1] and experiment for a few of the computed properties. They present both the systematic deviation of the DFT numbers and the remaining error bars:

cohesive energy: 0% deviation / 17 kJ/mol error bar
equilibrium volume: +4% deviation / 0.6 A^3/atom error bar
bulk modulus: -5% deviation / 9 GPa error bar

Although the major part of the error bars stems from the choice of a particular DFT functional, a sometimes non-negligible part of it is due to the computational approach, and is hence code-dependent. The same test set of elemental crystals can provide insight into this aspect as well. A quality factor Delta has been defined to compare the equations of state for different codes directly. This quantity expresses the rms energy deviation between the E(V) curve of a code under test, and that of the APW+lo code WIEN2k [2], averaged over the entire test set. WIEN2k is an all-electron method, believed to provide results that are as close as possible to the true results for the chosen functional. For VASP a Delta of 2 meV/atom was found, while for GPAW [3], a similar grid-based code, it was 3 meV/atom.

References

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