Towards reliable calculations of binding energies of molecular solids

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Density functional theory (DFT) methods are widely used to study properties of molecular solids. This is due to the manageable computational cost of the calculations and acceptable accuracy. This is true also for calculating properties of polymorphs. However, it is also known that part of the success of DFT when applied to, e.g., calculation of energy differences between polymorphs comes from error cancellations.

I will present the results of our calculations in which we aim to obtain reliable energy differences between polymorphs and understand the errors of DFT and other widely used or emerging methods. Specifically, we use many-body expansion (MBE) of the binding energy to obtain binding energy contributions from dimers, trimers, and larger clusters at the reference-quality level. We then use these datasets to assess simpler schemes, including different dispersion-corrected DFT functionals.

Because the computational cost of the reference-quality methods quickly grows with the system size these tests are necessarily limited to molecules with up to around ten atoms. To study larger molecules, reduced scaling approaches, so-called local coupled cluster (LCC) methods, have been proposed. These offer a way to obtain reference MBE contributions. I will show that this is not straightforward and we will present how the precision of LCC needs to be controlled to obtain various MBE contributions for different expected levels of precision.

Finally, I will discuss how numerical settings of the calculations can affect the predicted properties. For example, how the choice of projector-augmented wave data sets in plane-wave codes changes the binding energies for different systems and how the choice can affect optimized structures.