Understanding the accuracy of random phase approximation for binding energies

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The random phase approximation (RPA) with singles corrections (RSE or *GW* SE) was shown to give binding energies of molecular solids within only a few percent of the reference values [1]. However, comparison to a single number can be misleading as the good performance can be result of a favourable cancellation of errors. To understand the binding energies of RPA in detail we employed many-body expansion (MBE) in which the binding is divided into contributions of molecular dimers and corrections from higher-body terms. We performed MBE for binding energy of methane in water clathrate [2] and for crystals of short hydrocarbons [3]. Apart from PBE input states, used in [1], we also used SCAN and the hybrid variants of both functionals.
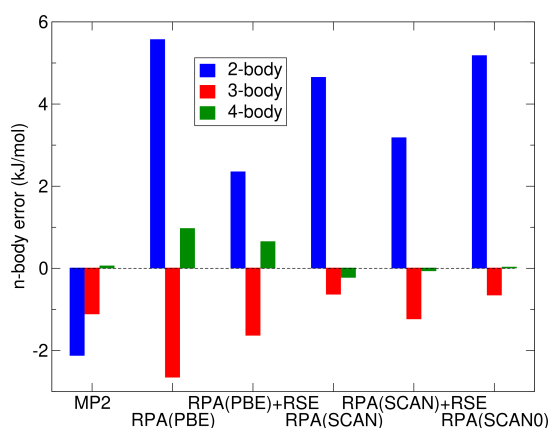

Figure 1: Errors of many-body energies of different methods for ethylene crystal.

We find that PBE- and SCAN-based RPA often lead to similar binding energies, the difference is less than 0.1 kJ/mol for ethylene and around 0.5 kJ/mol when RSE are included. However, their many-body errors substantially differ, as shown in the figure. Specifically, the 3- and 4-body errors are larger in magnitude for PBE- and PBE0-based RPA than when SCAN or SCAN0 input is used. As a result, there is substantially more error cancellation between the different MBE orders for PBE-based RPA than there is for RPA(SCAN). The larger 3- and 4-body errors of RPA(PBE) are a consequence of larger many-body errors of the PBE functional. Compared to MP2, RPA leads to more consistent errors across the different systems. However, MP2 has usually very small 4-body errors which we ascribe to the use of Hartree-Fock input states.

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