Regularized second-order energy expressions in context of post-HF and KS-DFT.

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ABSTRACT

Møller-Plesset second-order (MP2) perturbation energy expression has been a workhorse for quantum chemistry methods for many years. It has been widely utilized in the post-Hartree-Fock (post-HF) calculations and Kohn-Sham density functional theory (KS-DFT) to define various classes of functionals, i.e., double hybrids. Although the list of successful applications of the MP2 method is quite long, it suffers from many limitations, i.e., divergence in the cases where HOMO-LUMO energy gap closes, metallic systems, and large $\pi - \pi$ stacking systems. In this work, we analyze several possible forms of regularization of MP2 energy expression in the context of post-HF and KS-DFT calculations to show the advantages and disadvantages of these formulas. Our analysis concentrates primarily on some model systems where standard second-order energy expression fails badly, i.e., stretched H_2 molecule, Hook's atom model, and homogeneous electron gas. We will demonstrate some numerical results proving that none of the investigated regularized schemes fully resolve all known problems related to the second-order correlation energy expression in both contexts.

References

[1] Sawicki, I.; Triglione, V.; Jana, S.; Śmiga, S. A thorough analysis of regularized second-order energy expressions. What do we gain, and what do we lose? (Submitted)