Analysis of 2nd order Görling-Levy energy-based functionals with error decomposition

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ABSTRACT

The highest rung of Jacob's ladder of density functional approximation (DFA) contains a large group of exchange-correlation functionals that incorporate the second-order correlation energy expression in their formula, i.e., ab initio DFT, double hybrids (DH) or Adiabatic Connection Integrand Interpolation (ACII) approximations. Although the full Kohn-Sham realization of these functionals is possible[1,2] via the optimized effective potential (OEP) method, it is usually avoided due to problems in realizing the latter. In practice, the calculation with DH and ACII DFAs are done by feeding their energy expressions with orbital and eigenvalues, usually precomputed at the hybrid level obtained within the generalized Kohn-Sham (GKS) scheme. As shown in [1,3] the final results can significantly vary depend on the choice of reference orbitals for these types of DFAs.

We have performed the analysis of all the above DFAs [3] by means of density-(DD) and functional-driven (FD) error decomposition [4]. To this end, we utilized several choices input quantities (orbitals and eigenvalues), taking as a reference the nearly exact WY[CCSD(T)] Kohn-Sham orbitals and eigenvalues obtained from the CCSD(T) relaxed density matrix.

The error decomposition demonstrates that the accuracy of DFAs is significantly burdened by FD error, which dominates the results once nearly exact reference data are used. We have also demonstrate that for certain choices of orbitals, the DD error can reduce the total error by the mutual error cancellation effect with the FD counterpart. Moreover, we show that DH DFAs usually benefit from GKS realization, whereas full OEP realization leads to a lack of convergence in many cases. The analysis also reveals a clear path to improve all second-order-based types of approximation.

References

[1] Śmiga et al. J. Chem. Phys. 145, 144102 (2016)

[2] Śmiga et al. J. Chem. Theory Comput. 18, 10, 5936 (2022)

[3] Fabiano et al. J. Chem. Theory Comput., 12, 10, 4885 (2016)

[4] Kim et al. Phys. Rev. Lett. 111, 073003 (2013)

[5] Singh et al. (submitted)