Minimally Empirical Double-Hybrid Density Functional Theory: G4-level accuracy at DFT+ cost

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We have shown[Isr. J. Chem. 60:787-804 (2020) and refs. therein] that, for large and chemically diverse benchmark suites like GMTKN55 [PCCP 19:32184-32215 (2017)], double hybrid density functional theory can reach performance levels historically associated with composite wavefunction theory methods, and that it can do so with only a modicum of empiricism. In terms of further improvement, we find [J. Phys. Chem. A 125:4614-4627 (2021)] that range separation in the exchange does not benefit GMTKN55 much, though we do find it beneficial for some other applications. Somewhat to our surprise [J. Phys. Chem. A 125:4628-4638 (2021)], we did not see a major benefit to replacing PT2 correlation with dRPA, although it allowed for reducing both the number of parameters further and removing virtually all sensitivity to the underlying semilocal exchange-correlation functional. Using an addition third-order correction in a basis of Kohn-Sham orbitals does help matters further when the PT3 term is evaluated in a basis of Kohn-Sham orbitals. With this so-called XYG9 functional, we were able [J. Phys. Chem. Lett. 12:9368-9376 (2021)] to bring down WTMAD2 (weighted mean absolute deviation) to just 1.17 kcal/mol, comparable to the best composite wavefunction schemes. If a slightly higher WTMAD2=1.42 is acceptable, both dispersion correction and post-LDA corrections in the underlying orbitals can be eliminated.

In an attempt to address the slower basis set convergence of double hybrids, we have considered evaluating the PT2 contribution by F12 explicitly correlated approaches, and additionally to use localized pair natural orbital approximations to reduce CPU time scaling with system size. We found [J. Chem. Theory Comput. 18:5978–5991 (2022); J. Phys. Chem. Lett. 13:9332–9338 (2022)] that even the small cc-pVDZ-F12 basis set is as close to the basis set limit as cc-pV5Z in a conventional double hybrid, and that the LPNO approximation does not perceptibly reduce accuracy.