W4 vs. Wn-F12 Theory: What Does Explicitly Correlated Coupled Cluster Theory Bring To The High-Accuracy Thermochemistry Table?

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We consider whether it is worthwhile to replace the valence CCSD step in Wn theory by CCSD-F12b or CCSD(F12*) in smaller basis sets.[1] In order to have a better reference, we have recalculated the valence CCSD parts of the 200-molecule W4-17 thermochemistry benchmark[2] through extrapolation from the AV{6,7}Z+d basis set pair. In the process, we found that the AV{5,6}Z+d pair normally used in W4 theory suffers from radial overcontraction for some second-row elements. For systems dominated by dynamical correlation, the CCSD-F12b and CCSD(F12*) methods both come very close to the benchmark using the smaller V5Z-F12 basis set,[3] drastically reducing mass storage and memory requirements compared to AV6Z+d. However, in molecules with strong static correlation like ozone or BN, not only does CCSD-F12b yield unacceptable errors even with basis sets as large as aug-cc-pwCV5Z, but even the more rigorous CCSD(F12*) exhibits significant differences from the CCSD limit. Through multiple perturbation theory analysis,[4] we were able to trace these differences to fourth-order coupling terms between the orbital doubles and geminal amplitudes. Overall, CCSD(F12*) has the smoothest convergence.

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