**Do CCSD and Approximate CCSD-F12 Variants Converge to the Same Basis Set Limits? The Case of Atomization Energies**

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Basis set convergence of computed thermochemical properties is dominated by the CCSD contribution: (T) converges considerably faster [1], while higher-order correlation effects converge ever more rapidly as one ascends the coupled cluster hierarchy [2]. Approximate CCSD-F12 methods offer greatly accelerated basis set convergence over conventional CCSD. From purely theoretical arguments, CCSD and CCSD-F12 without approximations must converge to the basis set limit; however, the truth is more complicated for *approximate* F12 methods and *practical-sized finite* (one-particle) basis sets. To shed further light on this issue, the convergence to the basis set limit of CCSD (coupled cluster theory with all single and double excitations) and of different approximate implementations of CCSD-F12 (explicitly correlated CCSD) has been investigated in detail[3] for the W4-17 thermochemical benchmark[4]. $L \leq 7$ was considered in the conventional, and $L \leq 5$ in the explicitly correlated calculations. Near the CBS ([1-particle] complete basis set) limit, CCSD and CCSD(F12∗) agree to within their respective uncertainties due to residual basis set incompleteness error (about ±0.04 kcal/mol), but a nontrivial difference remains between CCSD(F12∗) and the popular CCSD-F12b model even for basis sets as large as cc-pV5Z-F12 [5]. Said difference is roughly proportional to the degree of static correlation as gauged by various diagnostics. Combining empirical observations with an earlier multiple perturbation analysis[6], we learn that the observed basis set convergence behavior results from the superposition of a rapidly converging, attractive, CCSD[F12]–CCSD-F12b difference (consisting mostly of third-order terms) and a more slowly converging, repulsive, fourth-order difference between CCSD(F12∗) and CCSD[F12]. For accurate thermochemistry, we recommend CCSD(F12∗) over CCSD-F12b if at all possible. There are some indications that the nZaPa family of basis sets[7] exhibits somewhat smoother convergence than the correlation consistent family.
As a by-product, we obtain a slight revision of the W4-17 reference values.

**References**

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