

# Dispersion-F12: Converging Symmetry-Adapted Perturbation Theory Data to the Complete Basis Set Limit with Explicit Correlation

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The symmetry-adapted perturbation theory (SAPT) approach to intermolecular interactions provides both accurate total interaction energies and their decomposition into physical contributions due to electrostatics, induction, dispersion, and exchange. As different contributions are obtained independently, they can be computed using different basis sets. It has been observed that while the leading electrostatic, exchange, and induction SAPT terms converge rather quickly (similar to the Hartree-Fock method), the dispersion contribution, arising entirely due to electron correlation, shares the slow basis set convergence with other correlated approaches such as MP2 or CCSD(T). Fortunately, the techniques used to improve the slow convergence of e.g. supermolecular CCSD(T) interaction energies, such as midbond functions and the explicitly correlated (F12) treatment, are also applicable to SAPT dispersion terms. To this end, following previous partial developments [1, 2], we have derived and implemented the F12 extensions of the leading SAPT dispersion and exchange-dispersion terms,  $E_{\text{disp}}^{(20)}$ -F12 and  $E_{\text{exch-disp}}^{(20)}$ -F12 [3]. Similar to the MP2-F12 and CCSD-F12 approaches, explicitly correlated SAPT becomes competitive with the conventional one only when robust density fitting (DF) is used to break down all four-index quantities. We have derived and implemented [4] the resulting DF- $E_{\text{disp}}^{(20)}$ -F12 and DF- $E_{\text{exch-disp}}^{(20)}$ -F12 expressions within the PSI4NUMPY framework [5]. This enabled us to test the basis set convergence of the F12 dispersion treatment on a large variety of popular noncovalent databases. Comparisons to the most accurate benchmarks on the A24 dataset show that DF- $E_{\text{disp}}^{(20)}$ -F12 and DF- $E_{\text{exch-disp}}^{(20)}$ -F12 computed in aug-cc-pVXZ basis set exhibit similar accuracy as their conventional counterparts computed in aug-cc-pV(X + 2)Z, and even further convergence enhancement is afforded by the addition of midbond functions. The effects of improved basis set convergence on the accuracy of total SAPT energies are varied: at the lowest SAPT0 level, the F12 influence is detrimental as error cancellation is disturbed. At higher levels of SAPT, including the F12 terms eliminates one of the leading error sources and has a strongly beneficial effect on the accuracy of, say, SAPT2+3(CCD) $\delta$ MP2 in the aug-cc-pVDZ basis.

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