

Dispersion Energy of Symmetry-Adapted Perturbation Theory from the Explicitly Correlated F12 Approach

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Methods of the explicitly correlated F12 approach are applied to the problem of calculating the uncoupled second-order dispersion energy, $E_{\text{disp}}^{(20)}$, in symmetry-adapted perturbation theory (SAPT). The accuracy of the new method is tested for noncovalently bound complexes from the A24 data set [1] using standard orbital basis sets aug-cc-pVXZ supplemented with auxiliary aug-cc-pVXZ_OPTRI sets [2]. For near equilibrium geometries, it is possible to recover the dispersion energy with average relative errors consistently smaller than 0.1% (with respect to the CBS extrapolated limit estimated from regular orbital calculations). This level of accuracy is achieved already in the basis set of a triple- ζ quality, when a Slater-type [3] correlation factor $\exp(-0.9r_{12})$ is combined with variant C of the F12 approach. The explicitly correlated approach clearly outperforms regular orbital calculations in the basis set of quintuple- ζ quality (average relative errors of 1%).

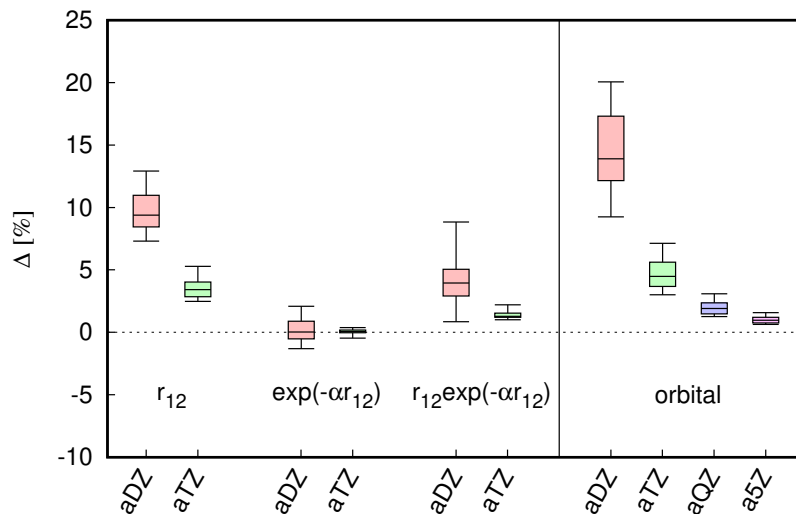


Figure 1: Relative percent errors of the $E_{\text{disp}}^{(20)}$ calculated for dimers from the A24 data set. [4]

References

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