

Explicitly Correlated Local Coupled Cluster Methods using Pair Natural Orbitals

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Well parallelized explicitly correlated local coupled-cluster methods using pair natural orbitals, PNO-LCCSD(T)-F12 [1–4], are presented. To reduce the size of the virtual space, the methods use successive transformations of the canonical virtual orbitals via projected atomic orbitals (PAOs) and orbital specific virtual (OSVs) to pair natural orbitals (PNOs) with local domain approximations. The inclusion of explicit correlation (F12) terms can significantly reduce the errors caused by these domain approximations. A hierarchy of strong, close, weak, and distant correlated orbital pairs was introduced, which greatly improved the description of long-range interactions over previous local coupled cluster methods. Asymptotically, the method scales near linearly with the number of correlated electrons. Accurate PNO-LCCSD(T)-F12 calculations for three-dimensional molecules with ~ 200 atoms using augmented triple- ζ basis sets can be carried out in a few hours of elapsed time.

Extensive benchmarks for reaction energies and intermolecular interaction energies are presented, in which the convergence of the results with respect to local approximations is studied [4]. For most of the case studied, the errors of relative energies due to local approximations are expected to be below 1 kcal/mol. When applied to the S66 set of intermolecular interaction energies, PNO-LCCSD(T)-F12 calculations using the aug-cc-pVTZ-F12 basis set yield results with root mean square deviation only 0.024 kcal/mol from the currently best CCSD(T)/CBS estimates [5].

Recently implemented high-spin open-shell coupled-cluster methods PNO-RCCSD and PNO-UCCSD is also presented [6]. The PNOs for open-shell molecules are obtained from semi-canonical spin-adapted restricted Møller-Plesset perturbation theory using large PAO domains [7]. Only a single set of PNOs are required for each pair, which leads to a similar cost of integral transformation as in the closed-shell case. The spin-orbital based CCSD equations are then solved with the hierarchy of pair approximations. The methods show accuracy comparable to the closed-shell PNO-LCCSD method in benchmark tests on ionization energies and radical stabilization energies.

References

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