Basis Set Limit CCSD(T) Energies for Extended Molecules via a Reduced-Cost Explicitly Correlated Approach

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Several approximations are introduced and tested to reduce the computational expenses of the explicitly correlated coupled-cluster singles and doubles with perturbative triples [CCSD(T)] method for both closed and open-shell species. First, the well-established frozen natural orbital (FNO) technique is adapted to explicitly correlated CC approaches. Second, our natural auxiliary function (NAF) scheme is employed to reduce the size of the auxiliary basis required for the density fitting approximation regularly used in explicitly correlated calculations. Third, a new approach, termed the natural auxiliary basis (NAB) approximation, is proposed to decrease the size of the auxiliary basis needed for the expansion of the explicitly correlated geminals. The performance of the above approximations and that of the combined FNO-NAF-NAB approach are tested for atomization and reaction energies. Our results show that overall speedups of 7-, 5-, and 3-times can be achieved with double-, triple-, and quadruple-ζ basis sets, respectively, without any loss in accuracy. The new method can provide, e.g., reaction energies and barrier heights well within chemical accuracy for molecules with more than 40 atoms within a few days using a few dozen processor cores, and calculations with 50+ atoms are still feasible. These routinely affordable computations considerably extend the reach of explicitly correlated CCSD(T).