An efficient linear-scaling CCSD(T) method based on local natural orbitals

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An improved version of our general-order local coupled-cluster (CC) approach [1] and its efficient implementation at the CC singles and doubles with perturbative triples [CCSD(T)] level is presented. The method combines the cluster-in-molecule approach of Li and co-workers [2] with frozen natural orbital (NO) techniques. To break down the unfavorable fifth-power scaling of our original approach a two-level domain construction algorithm has been developed. First, an extended domain of localized molecular orbitals (LMOs) is assembled based on the spatial distance of the orbitals. The necessary integrals are evaluated and transformed in these domains invoking the density fitting approximation. In the second step, for each occupied LMO of the extended domain a local subspace of occupied and virtual orbitals is constructed including approximate second-order Møller–Plesset NOs. The CC equations are solved and the perturbative corrections are calculated in the local subspace for each occupied LMO using a highly-efficient CCSD(T) code, which was optimized for the typical sizes of the local subspaces. The total correlation energy is evaluated as the sum of the individual contributions. The computation time of our approach scales linearly with the system size, while its memory and disk space requirements are independent thereof. Test calculations demonstrate that currently our method is one of the most efficient local CCSD(T) approaches and can be routinely applied to molecules of up to one hundred atoms with reasonable basis sets.

[1] Z. Rolik, M.Kállay *J. Chem. Phys.*, 135:104111, 2011.

[2] W. Li, P. Piecuch, J. R. Gour, S. Li *J. Chem. Phys.*, 131:114109, 2009.