Reduced Scaling CCSD(T) : Wavefunction Compression in Thermochemistry

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Coupled cluster singles and doubles with perturbative triples, the famous CCSD(T), has long been used in a wide array of quantum chemical studies. Of particular note is its employment as a key component in high-accuracy composite model chemistries that achieve sub kJ mol^{-1} accuracy, including HEAT, Wn, FPD, FPA, and others. The $O(N^7)$ scaling of the non-iterative triples correction permits a treatment of the T_3 excitation operator with basis sets large enough to provide the accuracy that these schemes aim to achieve. However, the cost of this term still presents a challenge for extending the range of chemical space that these model chemistries can address, especially in HEAT-like methods that avoid a separate treatment of core and valance correlation through CCSD(T).

This work reports on some of our efforts to reduce the scaling of the (T) part of CCSD(T). By combining various tensor compression/factorization techniques, including Density Fitting of ERIs[1], Rank-Reduction of T_2 amplitudes[2], Tucker-3 compression of T_3 amplitudes[3], Laplace Transform of the orbital eigenvalue denominators[4], and Orthogonal Rotation of the Z_3 residuals[5], we demonstrate five different methods to reduce the scaling of (T) from $O(N^7)$ to $O(N^6)$. We further benchmark these scheme's performance in a subset of reaction energies generated from species in the W4.17 test-suite. Ultimately, all five schemes are capable of obtaining sub 0.1 kJ mol^{-1} error vs their canonical DF-CCSD(T) counterpart while maintaining reduced cost, making them promising candidates for new versions of high-accuracy model chemistries that aim to extend their range to medium-sized molecules. Some preliminary comparisons of the various schemes are discussed, along with some guidelines for their inclusion in model chemistries.

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