

THC-MP3: Practical Crossover and Investigation of Amplitude Fitting Errors

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The Tensor Hypercontraction (THC) factorization of the molecular integrals allows for a reduced-scaling implementation of methods such as MP2 and MP3, where substitution of the THC-factorized integrals along with a similar decomposition of the orbital energy denominators (e.g. Laplace quadrature) enables a topological factorization into terms scaling as $\mathcal{O}(n^3)$ or $\mathcal{O}(n^4)$. Paired with a further DF/RI/CD approximation the integral fitting also scales formally as $\mathcal{O}(n^4)$. This has been shown to be a potentially very effective strategy for MP2, and especially for SOS-MP2 in the AO basis which scales practically as $\mathcal{O}(n^3)$ or less. However, the double-Laplace quadrature required for (THC-DF-)MP3 leads to an extremely high prefactor and crossover with canonical DF-MP3 in the thousands of electrons.

Lee et al. recently showed that explicitly fitting the first-order doubles amplitudes avoids this high prefactor by moving the double Laplace quadrature into a single quadrature applied to only $\mathcal{O}(n^3)$ steps. Here, we present a partially-optimized version of this technique that achieves crossover with canonical DF-MP3 around 300 electrons. More importantly, we extend the first-order fitted MP3 method into a series of THC-MP3 methods that clearly illustrate the numerical effect of amplitude fitting, and also suggest possible strategies for mitigating this error in more complicated THC methods such as THC-CCSD for which amplitude fitting is mandatory. Finally we numerically examine the size-extensivity of THC methods.