Analytic energy gradients for high scaling terms in the couple-cluster singles and doubles method with density-fitting approximations

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Analytic energy gradients are necessary for finding optimized geometries of molecules, while fast evaluation of these gradients is a necessity for on-the-fly dynamics algorithms. In this work, analytic energy gradients are implemented for the coupled-cluster singles and doubles (CCSD) method with the electron repulsion tensor represented using density-fitting (DF) approximation. The DF approximation is efficient for the reduction of computational cost and storage required in the energy calculations using the coupled-cluster and related methods. Analytic energy gradients are already implemented for the DF-CCSD method. Here, we are approximating the steep scaling 2 particle density terms ($\Gamma_{cd}^{ab}, \Gamma_{ci}^{ab}$) using the DF approximations. The approximation is also applied for excited state energy gradient evaluation in the EOM-DF-CCSD method. Recently, it was realized that robust tensor hypercontraction (THC) approximation when applied to the steep scaling particle-particle ladder not only reduces the computational cost but also the improved accuracy with respect to other THC-CCSD variants. In this work, we have implemented this scheme to the analytic gradient evaluations. We analyzed the efficiency of this implementation on regular alkane chains.