Resolution-of-Identity and Cholesky Representations of Electron-Repulsion Integrals within Coupled-Cluster and Equation-of-Motion Methods: Go One More Mile

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A general implementation of of resolution-of-identity (RI) and Cholesky decomposition (CD) representation of electron-repulsion integrals within coupled-cluster with single and double substitutions (CCSD) and equation-of-motion (EOM) family of methods is presented[1]. The CCSD and EOM-CCSD equations are rewritten to eliminate the storage of expensive four-index intermediates leading to significant reduction in disk storage requirements, reduced I/O penalties, and improved parallel performance. In CCSD, the number of rate-determining contractions is also reduced; however, in EOM the number of operations is increased because the transformed integrals, which are computed once in the canonical implementation, need to be reassembled at each Davidson iteration. Nevertheless, for large jobs the effect of the increased number of rate-determining contractions is surpassed by the significantly reduced memory and disk usage leading to considerable speed-up. Overall, for medium-size examples, RI/CD CCSD calculations are approximately 40% faster than the canonical implementation, whereas timings of EOM calculations are twice faster. More significant speed-ups are obtained in larger bases, i.e., more than 2-fold speedup for CCSD and almost 5-fold speed-up for EOM-EE-CCSD in cc-pVTZ. Even more considerable speedups (6-7 fold) are achieved by combining RI/CD with frozen natural orbitals approach. The numeric accuracy of RI/CD approaches is benchmarked with an emphasis on energy differences. Errors in EOM excitation, ionization, or electron-attachment energies are less than 0.001 eV with typical RI bases and with 1e-4 threshold in CD. Errors with 1e-2/1e-3 thresholds, which afford more significant computational savings, are less than 0.04 and 0.008 eV, respectively.

[1] E. Epifanovsky, D. Zuev, X. Feng, K. Khistyaev, Y. Shao, and A.I. Krylov *J. Chem. Phys.*, submitted , 2013.