Performance of the two-determinant coupled-cluster method for triplet and open-shell singlet states of biradical molecules

Jesse J. Lutz[1,2], Marcel Nooijen[3], Ajith Perera[1], and Rodney J. Bartlett[1]

[1]Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA
[2]Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio 45433, USA
[3]Department of Chemistry, University of Waterloo, Waterloo, N2L 3G1, Ontario, Canada

We study the performance of the two-determinant (TD) coupled-cluster (CC) method, which, unlike conventional ground-state single-reference (SR) CC methods, can in principle provide a naturally spin-adapted treatment of low-spin singlet and high-spin triplet electronic states. Various choices for the TD-CC reference orbitals are considered, including those generated by the state-averaged complete active space self-consistent field method. Comparisons are made, where appropriate, with the results of SR-CC, SR equation-of-motion (EOM) CC, and multi-reference EOM-CC calculations [M. Nooijen et al., J. Chem. Phys. **140**, 091102 (2014)], performed on a large test set of over 100 molecules with low-lying open-shell singlet states. It is shown that in some cases where the EOMCC reference function is poorly described, TD-CC can provide a significantly better quantitative description of open-shell singlet total energies and singlet-triplet splittings. The quality of TD-CC properties and natural orbitals is also investigated.