Equation Of Motion Ansatz with Two Determinant Coupled Cluster Theory

Moneesha Ravi, Ajith Perera, Rodney J. Bartlett

Quantum Theory Project, University of Florida, Gainesville, Florida, USA

In Coupled-Cluster (CC) theory, excited states are usually obtained with Equation of motion (EOM) ansatz, among other approaches. This EOM ansatz is traditionally performed on a Single Reference Coupled Cluster (SRCC) reference wavefunction. Here, we perform EOM on a genuine Two Determinant Coupled Cluster (TDCC) reference wavefunction. We accomplish this by transforming the solved TDCC wavefunction into an SRCC form and performing EOM-CC with no change in the usual EOM-CC equations.

To test the theory, we obtain two-determinantal states, such as open-shell singlets and Ms=0 triplet states, using genuine TDCC theory and perform EOM to get target states. Ground and doubly excited states are obtained as target states using these low-spin open-shell states as the reference state. This strategy can be especially advantageous for obtaining doubly excited states and the ground state of molecules with two-by-two multi-reference character. We demonstrate the quality of the results with this strategy in comparison with traditional EOM-CC and other variants of EOM, such as DIP-EOM-CCSD and DEA-EOM-CCSD for doubly excited states and singlet-triplet gaps of two-by-two multi-reference molecules.