

Efficient Implementation and Applications of the Doubly Electron-Attached and Doubly Ionized Equation-of-Motion Coupled-Cluster Methods

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The full and active-space doubly electron-attached (DEA) and doubly ionized (DIP) equation-of-motion (EOM) coupled-cluster (CC) methods with up to 4-particle–2-hole ($4p-2h$) and 4-hole–2-particle ($4h-2p$) excitations, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated ground-state CC wave function of an N -electron closed-shell system in order to generate the ground and excited states of the related ($N\pm 2$)-electron species of interest, such as biradicals, have been developed [1,2]. In the case of the DEA approach, the active-space DEA-EOMCC($4p-2h$) method has been augmented by a more cost-effective model at the $3p-1h$ level, where both $3p-1h$ and $4p-2h$ terms are selected using active orbitals [3]. We have recently improved computational efficiency of our original DEA- and DIP-EOMCC codes through $4p-2h$ and $4h-2p$ excitations [1-3], so that we can now perform routine calculations for sizable molecular problems with ~ 50 – 100 electrons and larger basis sets at the highest theory levels including high-order $4p-2h$ and $4h-2p$ physics. Our plan is to incorporate our new DEA- and DIP-EOMCC routines in GAMESS. By examining the low-lying singlet and triplet states of methylene and trimethylenemethane biradicals, and bond breaking in F_2 , we demonstrate that the DEA- and DIP-EOMCC methods with an active-space treatment of $4p-2h$ and $4h-2p$ excitations reproduce the results of the analogous full calculations at the small fraction of the computer effort, while improving the DEA/DIP-EOMCC theories truncated at $3p-1h/3h-1p$ excitations and making the DEA/DIP-EOMCC results considerably less sensitive to the type of orbitals used in the calculations [1-3]. Using the above and several additional examples, including singlet–triplet gaps in a series of antiaromatic molecules [3,4] and three benzyne isomers [5], we show that our newest variants of the DEA-EOMCC approaches with an active space treatment of $3p-1h$ and $4p-2h$ excitations and its lower-level counterpart neglecting $4p-2h$ contributions are capable of accurately reproducing the results obtained using their relatively expensive parent counterparts with a full treatment of $3p-1h$ and full or active-space treatment of $4p-2h$ excitations at the small fraction of the computational effort. This work brings us one step closer to a situation, where we may be able to perform routine high-accuracy spin- and symmetry-adapted CC computations for multi-reference (MR) problems, such as those encountered when balancing high-spin and low-spin electronic states, without resorting to genuine MRCC theories.

References

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