On the Performance of Perturbative Triples Corrections in CC and EOM-CC for Open-Shell States: The Case of SnC

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The methodology for calculating the electronic structures of the low-laying states of the recently detected SnC is investigated. To answer if a single-reference (SR) approach is appropriate for describing these open-shell states we compare transition energies and potential energy curves via coupled-cluster (CC) and equation-of-motion CC (EOM-CC). The EOM-CC excitation energy (EE) and spin-flip (SF) variants employed in this study allow the description of multi-reference (MR) states. For accurate description, inclusion of triple-excitations is required, and the performance of the non-iterative schemes is the focus of this paper. The transition between the two low-laying SnC states, $^3\Pi \rightarrow {}^3\Sigma^-$, is used as a test case. A mixed approach of two EOM-CC variants, SF and EE, upon inclusion of the non-iterative (dT) triples correction [SF$-$EE(dT)] adequately describe this transition, in addition, it helps to reveal the origin of the EOM-EE-CCSD(dT) failure in this case. The SF and EE variants have mathematically equivalent expressions, and numerically the energies of a state (with different spin projection) calculated by the two variants are degenerate, therefore, it is appropriate to mix these two variants. We show that by using the same reference state SF$-$EE(dT) yields highly balanced transitions, e.g., $^3\Pi \rightarrow {}^3\Sigma^-$. SF$-$EE(dT) yields the best excitation among the perturbative triples schemes examined here, and their quality is equivalent to the ones obtained by the standard EOM-SF-CCSD(dT). Moreover, SF$-$EE(dT) allows the description of many states, where some are forbidden by the individual variants, thus extends the EOM-CC accessibility.

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