Equation-of-motion coupled cluster method with full inclusion of triple excitations for open shell systems

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A new version of the equation-of-motion coupled-cluster (EOM-CC) theory which completely includes the connected single, double and triple (SDT) excitations has been derived and implemented for the open shell systems. The method requires the construction of the transformed Hamiltonian operator, $\bar{H} = e^{-\hat{T}} H e^{\hat{T}}$, which subsequently is diagonalized within the appropriate subspace (SDT) of the configurational space.

The crucial point in the efficient formulation of the model is the elimination of all four-body and a part of the three-body components of the $\bar{H}$ through the factorization procedure. It is important to note that this procedure does not introduce any approximation and the method remains still rigorous. Due to this the approach could be applied to relatively large basis sets (ca. 150 functions when the spatial symmetry is considered).

Initial applications have been made to the evaluation of the vertical and adiabatic excitation energies of the acetylene cation (augmented triple zeta) and of the NH molecule (quadruple zeta basis set). The computed quantities agree well with experimental data (if available) and belong to the most accurate results in the literature.