Highlighting Potential Challenges in Time-Dependent Equation-of-Motion Coupled-Cluster Theory

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Recent years have seen an increasing interest in the usage of real-time time-dependent (TD) electronic structure methodologies. In particular, the TD variants of equation-of-motion (EOM) coupled-cluster (CC) approaches are appealing due to the properties that derive from their time-independent counterparts, such as their accuracy, rapid convergence to the exact limit as a function of the truncation in the cluster and EOM excitation operators, ease of implementation, and ability to model driven excitation phenomena. Nevertheless, truncated TD-EOM-CC approaches employ similarity-transformed Hamiltonian that are non-Hermitian and could be defective, resulting in unphysical behaviors such as complex eigenvalues in the vicinity of conical intersections and negative- or complex-valued oscillator strengths. Furthermore, even if such problems do not manifest, the reduced density matrices (RDMs) characterizing the eigenstates and TD-EOM-CC "wave functions" of similarity-transformed Hamiltonians may violate *N*-representability conditions, *i.e.*, these RDMs do not necessarily map to a physical *N*-electron state, which further complicates the rigorous interpretation of TD-EOM-CC simulations. In this work, we use EOM-CCSD calculations on model systems that exhibit the aforementioned problems and showcase how the subsequent TD-EOM-CCSD could potentially be affected.