*N*-Representability Errors in Truncated Equation-of-Motion Coupled-Cluster Methods

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Equation-of-motion (EOM) coupled-cluster (CC) is not a true wave function theory unless the many-electron basis set is complete. For example, for truncated EOM-CC methods, it is surprisingly easy to generate states whose reduced density matrices (RDMs) are not derivable from any physical *N*-electron state. In other words, these RDMs are not *N*-representable. We identify EOM-CC with single and double excitations (EOM-CCSD) stationary states whose one-electron RDMs (1RDMs) violate either ensemble-state *N*-representability conditions or pure-state conditions known as generalized Pauli constraints (GPCs). Unphysical states are also encountered in the course of time-dependent EOM-CC simulations. When an external field drives transitions between a pair of stationary states with pure-state *N*-representable 1RDMs, the 1RDM of the time-dependent state can violate ensemble-state conditions. These observations point to potential challenges in interpreting the results of time-dependent EOM-CCSD simulations.