Equation-of-motion internally contracted multireference unitary coupled-cluster theory

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The accurate computation of excited states remains a challenge in electronic structure theory, especially for strongly correlated systems. In this paper, we present a novel extension of the equation-of-motion coupled-cluster theory, founded upon an internally contracted multireference unitary coupled-cluster singles-and-doubles framework (ic-MRUCCSD), namely EOM-ic-MRUCC. EOM-ic-MRUCC follows the transform-then-diagonalize route, like its non-unitary counterpart (MR-EOMCC) formulated by Datta and Nooijen [J. Chem. Phys. **137**, 204107 (2012)]. In EOM-ic-MRUCC, the transform step captures all dynamical correlation for the parent state, making the ground state energy size-extensive. Three excitation manifolds were tested in the subsequent diagonalization step. We found that size-intensive excitation energies can be achieved if all excitation operators satisfy the vacuum annihilation condition. Excitation energy curves of the BeH_2 model system and the symmetric dissociation of the water molecule deviate from the full configuration-interaction results by less than 2 mE_h for excited states within 0.5 E_h of the ground state.