Active-Space Equation-of-Motion Coupled-Cluster Methods for Ground and Excited States of Radicals and Other Open-Shell Species

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The electron-attached (EA) and ionized (IP) equation-of-motion coupled-cluster (EOMCC) methods, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated, ground-state, CC wave function of an \(N\)-electron closed-shell system in order to generate the ground and excited states of an \((N\pm1)\)-electron system, and their symmetry-adapted-cluster configuration interaction (SAC-CI) counterparts, provide an ideal framework for performing orthogonally spin-adapted calculations for radical species. The problem with these approaches is that their basic, low-order approximations are often insufficient for accurately describing excited states and potential energy surfaces along bond-breaking coordinates of radicals, and so higher order excitations must be accounted for.\(^1\)\(^-\)\(^4\) Unfortunately, the inclusion of higher order excitations in the EA- and IP-EOMCC and SAC-CI schemes makes the resulting calculations prohibitively expensive, restricting the use of these approaches to relatively small systems and basis sets. To deal with this difficulty, we have recently developed the active-space variants of the EA- and IP-EOMCC\(^1\)\(^-\)\(^3\) and SAC-CI\(^4\) methods, in which one considers only small subsets of all higher-than-double, higher than 2-particle-1-hole (\(2p1h\)), and higher than 2-hole-1-particle (\(2h1p\)) excitations in the cluster, electron-attaching, and ionizing operators, respectively, which are selected through the use of a suitably defined set of active orbitals. In this presentation, we will discuss the fundamental theoretical aspects of the active-space EA- and IP-EOMCC and SAC-CI methodologies. We will then focus on the efficient computer implementation of the active-space EA- and IP-EOMCC methods including up to \(3p2h\) and \(3h2p\) excitations, referred to as EA- and IP-EOMCCSDt,\(^1\)\(^-\)\(^3\) and active-space SAC-CI methods including up to \(4p3h\) and \(4h3p\) excitations.\(^4\) In order to illustrate the performance of the resulting approaches, we will present the results of calculations for the adiabatic and vertical excitation energies and potential energy surfaces of the low-lying states of several radicals, including CH, OH, SH, C\(_2\)N, CNC, N\(_3\), and NCO.\(^1\)\(^-\)\(^5\) These calculations reveal that active-space methods with up to \(3p2h\) and \(3h2p\) terms provide accurate results for excited states within the Franck-Condon region while active-space methods with up to \(4p3h\) and \(4h3p\) terms are needed to accurately describe potential energy surfaces of radicals along bond breaking coordinates. Furthermore, the calculations show that the active-space schemes are capable of producing results that are virtually identical to those produced by their expensive parent EA- and IP-EOMCC and SAC-CI schemes with \(3p2h3h2p\) and \(4p3h4h3p\) excitations at a fraction of the computational cost.