Recent progress in the active-space electron-attached and ionized equation-of-motion coupled-cluster methodologies

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The active-space coupled-cluster (CC) and equation-of-motion (EOM) CC methods, in which higher-order components of the cluster and excitation operators are selected via active orbitals, represent the most straightforward way of incorporating multi-reference (MR) concepts within the CC framework [1]. At the same time, the most natural way of describing electronic structure of radicals and biradicals, and other valence systems around closed shells is provided by the electron-attached (EA) and ionized (IP) EOMCC theories, and their multiply attached and multiply ionized extensions. This talk will discuss our recent contributions to the EA/IP and active-space EOMCC methodologies, including the development of the doubly electron-attached (DEA) and doubly ionized (DIP) EOMCC theories with up to 4-particle-2-hole (4p2h) and 4-hole-2-particle (4h2p) excitations, and their inexpensive active-space variants that provide high accuracies of the full 4p2h/4h2p treatment with the CPU steps that scale as steps of CCSD times small prefactors [2]. The discussion of the key formal concepts will be augmented by the examples of benchmark calculations and selected molecular applications, including bond breaking, low-lying electronic states of radicals, and singlet-triplet and singlet-singlet gaps in biradical systems. The extension of the active-space ideas to the EA/IP, DEA/DIP, and similar EOMCC theories may bring us one step closer to a situation, where we may be able to perform accurate, straightforward, relatively inexpensive, and spin- and symmetry-adapted CC computations for some of the most typical MR problems without resorting to the complicated steps of the genuine MRCC theories.

[1] Piecuch, P. *Mol. Phys.*, 108:21(22,23)-2987, 2010, and references therein.
[2] Shen, J., Piecuch, P. *J. Chem. Phys.*, 138:19-194102, 2013.