Quantifying and reducing spin contamination in algebraic diagrammatic construction theory of charged excitations

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Many electronic structure methods rely on Hartree-Fock (HF) theory to provide reference orbitals for calculating accurate electron affinities (EA) and ionization potentials (IP). One of those methods is algebraic diagrammatic construction theory (ADC), which provides a computationally efficient approach for calculating accurate EAs and IPs. For open-shell systems specifically, ADC relies on an unrestricted HF (UHF) reference that can be plagued with spin contamination (SC) error, in which the wavefunction is not a true eigenfunction of the spin squared operator, $\hat{S}^2$. In this work, we assess the accuracy of ADC by calculating EAs and IPs for many open-shell molecules with different degrees of SC in the ground electronic state. Following this assessment, we benchmark the accuracy of ADC combined with other types of reference orbitals, such as: 1) orbital-optimized Møller-Plesset perturbation theory (OMP) and 2) restricted open-shell HF (ROHF). Our results demonstrate that for strongly spin contaminated systems, both OMP and ROHF reference orbitals reduce the spin contamination and energy errors in the electron-attached and ionized states simulated using ADC.