Spin-Adapted Coupled Cluster for Arbitrary Open-Shell States

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Coupled cluster has emerged as the method of choice for treating dynamic correlation in molecules, with the desirable properties of size consistency and high accuracy relative to other methods of comparable cost. However, the problem of spin contamination arises when treating molecules with open shell character, and systems with strong static correlation have required a multireference treatment, introducing intruder states and problems of multiple parentage that have not yet been satisfactorily resolved. Using a normal-ordered *ansatz*, We generate spin-free coupled cluster equations for open shell reference states using a new implementation of a fermionic operator algebra and tensor contraction engine. The spin-adapted reference states are configuration state functions constructed from Hartree–Fock orbitals to incorporate the strong correlation due to spin coupling. We have generated equations for reference wavefunctions of one and two open-shell electrons, both in the triplet and singlet configurations, and in principle equations can be generated for arbitrary states of high or low spin. Initially, we focus on the normal-ordered *ansatz* with double excitations, restricted to linear terms (NO-LCCD), but with no contractions between amplitudes, higher order terms can be readily incorporated. These automatically generated equations represent a step towards a method that would ultimately leverage the benefits of coupled cluster for dynamic correlation onto states for which the treatment of strong static correlation is already included.