Finite Expectation Value Coupled Cluster Method

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The standard coupled cluster methods (CC) works well when the reference determinant dominates the exact (Full CI) wavefunction. However, its numerical quality rapidly declines as the quasi-degeneracy of the system becomes severer. In the worst case, the coupled cluster calculation failes to capture qualitative description of the system (e.g.,significantly overshoot the Full CI ground energy). It is widely recognized that we can avoid this difficulty by resorting to the multireference formalism or incorporating higher order excitations, both of which are often impractical even for small molecules. In this study, we propose an extension of the single referecence CC method in order that we can stably manipulate quasi-degenerate molecular electronic structure for the ground state as well as the excited states without significant increase in the computational requirements for the CC calculation.