

Recent Advances in Externally Corrected Coupled-Cluster Methods

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One of the most promising ways of improving the results of single-reference coupled-cluster (CC) calculations in multi-reference and strongly correlated situations is offered by the externally corrected CC (ec-CC) methodology. The ec-CC approaches are based on the observation that by solving the CC amplitude equations projected on the singly and doubly excited determinants for the one- and two-body clusters, T_1 and T_2 , respectively, in the presence of their exact three-body (T_3) and four-body (T_4) counterparts extracted from full configuration interaction (FCI), one obtains the exact T_1 and T_2 and, thus, the exact energy. This suggests that by using external wave functions capable of generating an accurate representation of T_3 and T_4 clusters, and subsequently solving for T_1 and T_2 , one should not only produce energies that are much better than those obtained with CCSD, but also substantially improve the results of the calculations providing T_3 and T_4 . We will examine the validity of the latter premise and, with the help of suitable theorems and numerical analysis [1], demonstrate that the truncated CI wave functions that are best suited for the ec-CC computations are those that efficiently sample the many-electron Hilbert space, without saturating the lower-rank excitation manifolds, especially the excitations through quadruples, too rapidly, while adjusting the singly through quadruply excited CI amplitudes to the dominant higher-than-quadruply excited contributions, such as those obtained with the selected CI model abbreviated as CIPSI and FCI Quantum Monte Carlo (FCIQMC) propagations. We will then discuss our recently developed CIPSI-driven [1] and FCIQMC-driven [2–4] ec-CC models. We will show that the resulting ec-CC approaches allow us to extract the exact, FCI, or near-exact electronic energetics in situations involving chemical bond dissociations [1,2], molecules beyond the reach of FCI [3], and strongly correlated systems that emerge in modeling metal–insulator transitions [4], where the traditional CCSD, CCSDT, CCSDTQ, etc. hierarchy breaks down, out of the initial CIPSI iterations or the early stages of FCIQMC propagations combined with the inexpensive polynomial steps similar to CCSD. If time permits, we will also briefly overview our new results in the area of the approximate coupled-pair methods, which belong to the oldest category of the ec-CC approaches using T_4 clusters extracted from the projected unrestricted Hartree–Fock wave function and which are capable of accurately describing strongly correlated systems by retaining selected $(T_2)^2$ diagrams in the CCSD amplitude equations [5].

References

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