Externally Corrected Coupled-Cluster Methods Using Selected Configuration Interaction and FCIQMC

Piotr Piecuch[1,2], Ilias Magoulas,[1,*] Karthik Gururangan,[1] J. Emiliano Deustua,[1,†] and Jun Shen[1]

[1]*Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*
[2]*Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA*

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. In the first part of this talk, we will examine the validity of the latter premise. In particular, we will show that there exist large classes of truncated CI wave functions for which the ec-CC approach using the T_3 and T_4 components extracted from CI does not improve the underlying CI calculations [1]. We will also show 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. Thus, in the second part of this talk, we will 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 with the help of the inexpensive polynomial steps similar to CCSD.

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[*] Present address: Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA.
[†] Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA.