Externally Corrected Coupled-Cluster Methods: Review and Recent Progress

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In the first part of this talk, we will embark on a journey to honor the life and work of the late Professor Josef Paldus. With Professor Paldus' passing earlier this year, our community has lost an extraordinary person and legendary scientist, whose seminal work on exploiting dynamical symmetries, resulting in the unitary group approach, and the introduction (with Professor Jiří Čížek) of the coupled-cluster (CC) theory to molecular electronic structure have revolutionized quantum chemistry. Many of us, including the presenter of this lecture, have lost a cherished friend, collaborator, and mentor. This talk is our humble tribute to Professor Paldus' exceptional life and contributions and his enduring impact on the work of a great many, including the presenter.

One of the topics that the presenter of this talk pursued with Professor Paldus between 1988 and 1996 is the externally corrected CC (ec-CC) methodology, which represents one of the most promising ways of improving the results of single-reference CC calculations in multi-reference and strongly correlated situations [1]. 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, non-CC, 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 [2], 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 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 CIPSI-driven [2] and FCIQMC-driven [3] eFormer member of the Piecuch group (defended his Ph.D. in 2021). Currently at Emory University.c-CC models and their performance in applications involving chemical

bond dissociations [2,3(a)], molecules beyond the reach of FCI [3(b)], and strongly correlated systems that emerge in modeling metal–insulator transitions [3(c)], where the traditional CCSD, CCSDT, CCSDTQ, etc. hierarchy breaks down. We also hope to touch upon our recent 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, capable of describing strongly correlated systems by retaining and/or scaling selected $(T_2)^2$ diagrams in the CCSD equations [4].

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