Simplified coupled cluster methods to model complex electronic structures

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In its standard single-reference formulation, the coupled-cluster model is one of the most accurate tools for describing dynamical electron correlation, as the hierarchy of approximations rapidly converges to the full configuration interaction solution. In the presence of quasi-degeneracies, the higher-order excitation terms are indispensable since low-level approximations do not provide a qualitatively correct structure of the wave function. The hierarchy of approximations based on the excitation level breaks down for systems featuring many correlated electrons, as found in complexes containing elements from the d- and f-block of the periodic table. Possible remedies dedicated to capturing strong electron correlation effects are, for instance, tailored coupled cluster methods or simplified coupled-cluster approaches, where the cluster operator is restricted to electron-pair states. We will discuss a specific flavor of CC approaches where the amplitudes can be derived from geminal-based approaches like the pair coupled cluster doubles (pCCD) ansatz. Furthermore, we will discuss the performance of various pCCD-based methods to capture dynamic electron correlation effects and to describe the electronic structures of both closed- and open-shell molecules.

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