Development of modern electronic structure methods on top of geminal-based approaches

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The compromise between the computational cost of quantum-many-body methods and their accuracy and reliability is a central issue in quantum many body physics and chemistry. Specifically in electronic structure theory, we require methods that allow us to efficiently describe the correlated motion of electrons. Typically, we distinguish between strongly- and weakly-correlated electrons. Numerical studies suggest that geminal-based approximations like the pair-Coupled Cluster Doubles (pCCD) method are suitable to accurately model systems where strong correlation is important [3], like molecules with stretched bonds [1] as well as complexes or clusters containing actinide atoms [2]. Common among all geminal-based approaches, pCCD, however, misses (some fraction of) the weak correlation energy. Therefore, *a posteriori* corrections are required that compensate this deficiency. Examples thereof are Configuration Interaction, Perturbation Theory, or (linearized) Coupled Cluster corrections. Here, we will scrutinize the performance of various pCCD-based methods in capturing weak (or dynamic) electron correlation effects. The accuracy of the presented hybrid approaches can be assessed using concepts of Quantum Information Theory that allows us to dissect inter-orbital correlations [4]. Specifically, we highlight how these orbital correlation measures can be extracted from CC-type wave functions.

References

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