

Coupled Pair Methods as Geometric Approximations to Coupled Cluster Methods

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The coupled electron pair approximation, or CEPA, is a family of quantum chemistry methods in which one linearizes the coupled cluster equations. Hoffman and Simons pointed out in 1988 that one can formulate a generally similar method as a geometric approximation to unitary coupled cluster theory. We refer to this method as the Unitary Newton Step, or UNS. In this work, we investigate the numerical performance of the UNS method for a variety of closed-shell reaction energies, revealing that it suffers from similar numerical instabilities as CEPA(0). To correct this shortcoming, we introduce self-consistent shifts to the Hamiltonian associated with other coupled pair methods. In the original coupled pair methods, these shifts improve numerical stability; we believe that their effect on the UNS method will inform what the connection is between UNS and CEPA(0)