Explicitly-correlated combined coupled-cluster and perturbation methods

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The so-called explicitly-correlated coupled-cluster methods (CC-R12) have been derived and implemented with up to quadruple excitations (CCSDTQ-R12) based on the complete diagrammatic equations. The efficient computer codes exploit spin, real-Abelian point-group, and index-permutation symmetries. They form a hierarchy of methods that converge rapidly to the full configuration interaction method at complete basis-set limit. We have also developed approximate methods that treat higher-order excitations with the Rayleigh–Schrödinger perturbation expansions, called CCSD-R12(2)$_{T/TQ}$, CCSD-R12(3)$_{T}$, CCSDT-R12(2)$_{Q}$, and CCSD(R12)(2)$_{T/TQ}$. The Λ-CCSD-R12, Λ-CCSD(R12), and Λ-CCSDT-R12 equations are implemented to realize those methods. They can describe the potential energy curves along single bond breaking quantitatively for the FH and H_2O molecules, and have uniform effectiveness in capturing basis-set truncation errors along the potential energy curves; for instance, the vibrational frequency of the FH molecule obtained by the CCSD-R12(2)$_{TQ}$ and CCSDTQ-R12 methods using the aug-cc-pVDZ basis set are 3954 and 3953 cm^{-1}, respectively, and agree with the observed (3961 cm^{-1}) within 10 cm^{-1}, while that by the CCSDTQ method is 3881 cm^{-1} which is far smaller.

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