Explicitly correlated wave function approaches based on the random phase approximation

Anna-Sophia Hehn[a], Christof Holzer[b], David P. Tew[c] and Wim Klopper[b]
[a]*University of Zurich, Zurich, Switzerland,*
[b]*Karlsruhe Institute of Technology, Karlsruhe, Germany,*
[c]*Max Planck Institute for Solid State Research, Stuttgart, Germany,*
anna.hehn@chem.uzh.ch

Explicitly correlated wave function approaches have emerged as standard remedy for the slow basis-set convergence inherent to all orbital-based correlation methods. Especially in connection with coupled cluster theory, the F12 ansatz using Slater type geminals has proven as powerful approach, reducing computational timings due to drastically decreased basis-set sizes and thus enabling quantitative accuracy at feasible computational cost [1]. Complementing the line of already established F12 variants, we present explicitly correlated wave function approaches based on the random phase approximation (RPA). Even though RPA was originally developed to treat excited states in the context of density functional theory, it was later on found to be a promising orbital-dependent correlation method for ground-state energies, both capturing long-range dispersion and being, in contrast to perturbative approaches, stable for small-gap systems [2]. We show that the presented explicitly correlated RPA variants can be derived based on the method's connection to coupled cluster theory and that the gained improvement regarding basis-set convergence is comparable to the performance of state-of-the-art explicitly correlated coupled cluster approaches [3,4,5].

References

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