# Dynamic Correlation for CASSCF Reference with Adiabatic Connection Approaches: Open Shell Systems and Dispersion Interaction

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Correlation energy, despite being a small fraction of the total electronic energy, governs binding of atoms into molecules. Similarly, noncovalent molecular interactions are flawed if the correlation of electrons belonging to interacting subsystems is not accounted for. Many-electron methods aim at predicting correlation energy of the short- and long-range type. The two main approaches to electron-correlation involve either perturbation theory or are based on density functionals. They are deficient either in accuracy or computational efficiency and a generally applicable, computationally efficient approach remains a challenge.

Recently we have proposed a novel approach to describing electron correlation in multireference systems by adopting the adiabatic connection (AC) formalism [1]. The latter naturally links electron correlation with fluctuation of density at different points in space. Consequently, the final expression for the correlation energy employs linear response properties. In our formalism, we use extended random phase approximation (ERPA) to describe the latter.

The proposed AC-ERPA method yields excellent results for ground and excited states of molecules described with the CASSCF wavefunction [2,3]. The AC and its inexpensive approximation AC0 method compete or surpass in accuracy the perturbation (PT2 or NEVPT2) corrections. Unlike the latter methods, the AC approximations do not require construction of higher than two-particle reduced density matrices.

AC methods have been extended to arbitrary spin symmetry of the reference CASSCF sate and successfully applied to open-shell systems [4]. Application of the AC0 method to description of tetramethyleneethane (TME) diradical reveals that that AC0 rather closely reproduces the FCIQMC benchmark for singlet and triplet states. It has also led to elucidation of the interplay of dynamic and static correlation as a decisive factor for understanding the shape of the diradical's potential energy surfaces.

**References**
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