Spin-violating geminal wave functions and their correction by petur-bation theory

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We review our work on strongly orthogonal two-electron functions (geminals) for capturing static correlation. Violation of geminal spin is admitted in order to overcome the shortcomings of the perfect pairing approximation in this framework. Performance of the geminal reference based correction step for describing dynamic correlation is a sensitive function of the extent of spin contamination. Breakdown of perturbation theory (PT) may be observed, analogously to the case of unrestricted Hartree-Fock based Moller-Plesset treatment.

We get around the problem by restoring the spin of the geminal product via full projection and half-projection (HP) with subsequent variation[1,2]. A necessary drawback of spin purification by projection, size-inconsistency is assessed in numerical terms. A further facet of projective schemes is the reference becoming a linear combination of geminal products, interfering with a geminal Hamiltonian based construction of the zero-order operator of PT. For this reason a dynamic correlation treatment, not assuming any special structure of the zero-order function, termed multi-configuration PT is investigated[3]. We also explore adopting the formalism of symmetry adapted PT (SAPT)[4], with HP playing the role of the symmetry operator involved[5]. Numerical tests on singlet-triplet gaps of biradicaloids illustrate the performance of the PT schemes.

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