Perturbative explicitly correlated basis set imcompleteness corrections

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Explicitly correlated R12 methods [1] are a means to overcome the slow convergence of the (dynamic) correlation energy of determinant-based methods with the size of the one-particle basis set. The well-known MP2-R12 method, already introduced at the beginning of R12 theory [2], treats the explicitly correlated part of the wave function together with the conventional doubly excited contributions as a part of the first-order perturbation theoretical wave function with the Hartree Fock wave function being of zeroth order. Here we present a generalization of perturbative explicitly correlated R12 theory at the level of state-of-the-art R12 theory [1] to other zeroth order wave functions based on the Löwdin partitioning technique [3]. The application of this method to CCSD, invoking further simplifications, is the CCSD(2)$_{\overline{\mathrm{R12}}}$ method [4] and it's fixed-coefficient version [5]. In the case of CCSD(T), we get the CCSD(T)$_{\overline{\mathrm{R12}}}$ method [6], considering the (T) and the $\overline{\mathrm{R12}}$ correction as perturbative corrections of CCSD. The advantage of these methods is that they are virtually as simple and computationally cheap as MP2-R12, still yielding about the accuracy of a conventional aug-cc-pV5Z calculation with an aug-cc-pVTZ orbital basis set. By employing a second quantization formalism for general multideterminantial wave functions [7], an universal perturbative explicitly correlated basis set imcompleteness correction applicable to any multideterminantial wave function yielding one- and two-particle density matrices can be derived with our approach [8]. By neglecting terms with higher-than two-electron cumulants [9] as well as terms, where two r_{12} matrix elements or one r_{12} and one g_{12} matrix element are connected via a two-electron cumulant [9], the $[2]_{\mathrm{R12}}$ correction [8] is obtained, yielding results with the quality of conventional aug-cc-pVQZ caculations with an aug-cc-pVDZ basis set in first tests [8]. The $[2]_{\mathrm{R12}}$ correction is internally contracted and employs state-of-the-art [1] R12 theory: when supplied with Hartree-Fock density matrices it recovers the explicitly correlated part of the projector 2 version of MP2-R12. With this, it is suited as a R12 correction to intricate wave functions, such as multireference configuration interaction.

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