

Pair coupled cluster doubles F12 approach.

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Surprisingly, recent works show that the extremely simple pair coupled cluster doubles (pCCD) wave function [1, 2] fairly well describes strong static electron correlation. Such a wave function is based on the ansatz

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle \quad (1)$$

with

$$\hat{T} = \hat{T}_p = \sum_{i,a} T_a^i \tilde{a}_{i\uparrow i\downarrow}^{a\uparrow a\downarrow}, \quad (2)$$

i. e. in this approximation to CCD only excitations of singlet pairs are allowed from a doubly occupied orbital to a virtual orbital. As noted in ref. [1], one can show that pCCD is equivalent to antisymmetrized product of one-reference-orbital geminals (AP1roGI) [3] belonging to the family of approximate antisymmetrized product of interacting geminals wave functions (APIG) [4]. Nonetheless, pCCD lacks an effective treatment of dynamical electron correlation. This fact inspired us to explore the combination of pCCD with explicit inclusion of dynamical electron correlation via the F12 approach as in CCSD-F12 [5], eventually with fixed cusp condition, known as SP-ansatz [6]. Then, \hat{T} in Eq. (1) is extended as:

$$\hat{\mathcal{T}} = \hat{T}_p + \hat{\mathcal{F}}. \quad (3)$$

$\hat{\mathcal{F}}$ is defined such that

$$\hat{\mathcal{F}}|\Phi\rangle = \left(1 - \sum_{i,a} \tilde{a}_{i\uparrow i\downarrow}^{a\uparrow a\downarrow} |\Phi\rangle \langle \Phi| \tilde{a}_{a\uparrow a\downarrow}^{i\uparrow i\downarrow}\right) \hat{\mathcal{R}}|\Phi\rangle, \quad (4)$$

where $\hat{\mathcal{R}}$ is a correlation factor –in our case Slater type geminal– operator normal ordered w.r.t. the reference $|\Phi\rangle$. We have also explored usefulness of optimized Thouless expansion approach [7] instead of orbital optimization.

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