On the performance of doubly occupied pairs coupled cluster doubles F12 approach.

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Inspired by the reported fair performance of the doubly occupied pair coupled cluster (pCCD) theory in describing the static electron correlation [1, 2, 3, 4] we have introduced and implemented its variant that includes single excitations and explicitly treats the dynamic electron correlation within the F12 methodology (pCCSD-F12). For such an approach the computation scaling is drastically reduced with respect to standard method using full double ecitation operator (CCSDF12) [5]. Slater type geminal as a correlation factor together with fixed cusp conditions were used, which is known as SP-ansatz. On the sample model systems, we have investigated the performance of reference states constructed either from canonical or localized molecular orbitals. Finally, the employment of Brueckner orbitals has been tested, when the single excitations naturally vanish from the wave function expansion (B-pCCD-F12). Our testing systems include increasing ring of hydrogen atoms, dissociation curves for small molecules such as HF, N_2 and CO_2 and comparison with the CCSD-F12 performance is presented for a series of reaction enthalpies.

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