

Explicitly correlated local coupled-cluster methods for large molecules

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We review our recent developments of explicitly correlated local coupled cluster methods for closed-shell and open-shell molecules. The virtual space is spanned by pair-specific domains of pair natural orbitals (PNOs), and weak correlations of distant electrons are treated by accurate pair approximations. Basis set incompleteness errors as well as errors caused by the domain approximations are strongly reduced by explicitly correlated (F12) terms. The closed-shell PNO-LCCSD(T)-F12 method [1-4] has been applied for computing reaction energies of numerous difficult systems with up to about 300 atoms and 10000 basis functions [4]. The method is well parallelized, and on small compute clusters such calculations can be carried out in a few hours of elapsed time. For smaller systems, typical errors relative to the corresponding canonical CCSD(T)-F12 method amount to less than 1 kJ/mol for reaction energies; for larger systems the accuracy can only be estimated by studying the convergence with respect to the domain sizes, and this indicates that also in large systems the local domain errors can be reduced to well below 1 kcal/mol. Errors caused by the weak pair approximations are generally negligible. Intermolecular interaction energies have been computed for the S22, S66, and X40 test sets, and the root mean square (RMS) errors relative to the best previous calculations amount to less than 0.05 kcal/mol [5]. Recently, the method has been extended to spin-orbital based open-shell PNO-RCCSD [6], based on spin-free PNOs obtained by a spin-restricted MP2 method [7]. In open-shell cases the accurate treatment of single excitations turns out to be more critical than for closed-shell calculations, and various approximations are compared. The method has been applied for computing ionization energies and radical stabilization energies, and the accuracy is found to be very similar as for closed-shell calculations. An extension to open-shell PNO-RCCSD(T)-F12 is in progress. Finally, we give an outlook to the treatment of large strongly correlated systems using new CASSCF [8] and (multi-state) PNO-CASPT2 [9,10] implementations. All described methods are available in the MOLPRO quantum chemistry program (version 2019.3).

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