Explicitly correlated coupled-cluster methods including triple and quadruple excitations

Mihály Kállay[1], **Réka A. Horváth**[1]

[1] Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O.Box 91, Hungary

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Recently, we have proposed a new approach to reduce the basis set incompleteness error of the triple excitation correction in explicitly correlated coupled-cluster (CC) singles and doubles with perturbative triples [CCSD(T)] calculations [1]. The approach, which is based on the orbital-specific scaling of the contributions of the perturbative triples correction, is size-consistent and significantly speeds up the basis set convergence of the triples correction. Here, we discuss its extension to the CC singles, doubles, triples (CCSDT) with perturbative quadruples [CCSDT(Q)] method. While the adaptation of the approach to the (Q) correction is straightforward, its extension to CCSDT is less trivial. We discuss several possibilities and assess their performance for total energies and energy differences. In addition, we also propose the extension of the more rigorous extended SP triple excitation ansatz of Köhn [2, 3] to CCSDT. We demonstrate that this approach results in a much more involved and expensive but more accurate explicitly correlated CCSDT method. It is also shown that the method can be considerably sped up with reasonable approximations.

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