Towards an efficient implementation of the multireference driven similarity renormalization group

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The nonperturbative version of the multireference driven similarity renormalization group (MRDSRG)[1] is a robust quantum chemistry method that is free from the intruder-state problem. However, our previous implementation is limited to about 250 orbitals due to the storage of four-index intermediates.[2] In this work, we propose a new method, termed SEQ-MRDSRG, that overcomes this limitation by combining the following techniques. Firstly, electron repulsion integrals are factorized using density fitting. Secondly, a sequential transformation approach[3] is applied to evaluating the MRDSRG Hamiltonian, which consists of two steps: (1) the effects of single substitutions are first folded exactly in via an efficient orbital rotation into the density-fitted integrals, and (2) doubles are considered using the Baker–Campbell–Hausdorff formula. Finally, we introduce the "non-interacting virtual-orbital" approximation to alleviate the storage requirement of four-index intermediates by ignoring all commutator contributions labeled by three or four virtual indices. A perturbative analysis shows that the leading error of this approximation appears in the fourth-order energy. We show that the SEQ-MRDSRG is capable of treating more than 400 virtual orbitals as accurately as the original MRDSRG theory.

References

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