Cumulant approximations in second-order multireference driven similarity renormalization group perturbation theory

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Accurate multireference electronic structure calculations are important for potential energy surface (PES) construction but limitations prevent their routine use. One of the most severe limitations is the high computational cost of post-CASSCF methods as the active space grows, especially due to the use of high-order density matrices. Two cumulant based approximations to high-order density matrices were previously investigated in strongly contracted second-order n-electron valence perturbation theory (SC-NEVPT2) [D. Zgid, D. Ghosh, E. Neuscamman, and G. K.-L. Chan, J. Chem. Phys. **130**, 194107 (2009)]. However, approximated forms of SC-NEVPT2 exhibit the intruder state problem and are less accurate than the parent theory. Our group proposed the second-order multireference driven similarity renormalization group perturbation theory (DSRG-MRPT2) in which the intruder state problem is resolved by replacing standard energy denominators with regularized ones. DSRG-MRPT2 only requires the three-body reduced density cumulant and, therefore, has a memory cost proportional to the six power of the number of active orbitals (n_{act}^6). To investigate reductions of the memory requirement of DSRG-MRPT2, we test four different levels of three-body reduced density cumulant approximations which set different classes of cumulant elements to zero. Our test cases show that additional error introduced by approximation can be made as small as 1 kcal/mol or less while the amount of memory required is reduced from $\mathcal{O}(n_{act}^6)$ to $\mathcal{O}(n_{act}^5)$.

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