

Reduced-scaling correlation methods for the excited states of large molecules

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A framework for the reduced-scaling implementation of excited-state correlation methods is presented [1]. An algorithm is introduced to construct excitation-specific local domains, which include all the important molecular orbitals for the excitation as well as for the electron correlation. The construction of the resulting compact domains can be performed with cubic scaling using the local density fitting approximation [2], and the sizes are further decreased utilizing our reduced-cost techniques developed based on the natural auxiliary function and local natural orbital approaches [3, 4]. Additional methodological improvements for the evaluation of density matrices are also discussed. The results of benchmark calculations performed at the second-order algebraic-diagrammatic construction level are presented, and it is demonstrated that the speedups achieved are significant even for systems of smaller than 100 atoms, while the errors introduced by our approximation are highly acceptable. Our results show that the new reduced-scaling algorithm allows us to carry out correlated excited-state calculations using triple- ζ basis sets with diffuse functions for systems of up to 300 atoms or 10000 atomic orbitals.

References

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