Large-scale v2RDM-driven CASSCF methods

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Abstract

Complete active-space self-consistent-field (CASSCF) methods are enormously important in electronic structure theory, as they allow for the description of the electronic states that are dominated by more than one electronic configuration. Unfortunately, most implementations of CASSCF are configuration-interaction (CI)-based, and the exponential scaling of CI severely limits the size of the active space that can practically be employed. The application of CASSCF to large active spaces requires that one abandon CI in favor of polynomial-scaling approaches such as the density-matrix renormalization group (DMRG) or variational two-electron reduced-density matrix (v2RDM) methods. Using a combination of state-of-the-art semidefinite programming techniques and density-fitting approximations, we have developed a computer implementation of a v2RDM-driven CASSCF procedure. Quantitative agreement with CI-based methods can be achieved through the application of partial three-particle N-representability conditions, while qualitative accuracy requires only the application of two-particle conditions. We use the approach to evaluate singlet-triplet gaps in a series of dinitrene diradicals and the linear acene series. Our largest computations consider active spaces with 50 electrons in 50 orbitals, while simultaneously optimizing more than 1800 orbitals.

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