

Combined first- and second-order CASSCF for large molecules

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The complete active space self-consistent-field (CASSCF) method enables the treatment of strong-correlation effects occurring for example in transition metal complexes. In the CASSCF method, both the orbitals and the configuration interaction (CI) coefficients of the multi-configurational wavefunction have to be optimized, and the method is numerically challenging through a strong coupling between orbitals and CI coefficients. Second-order CASSCF methods [1,2,3] show fast and reliable convergence for difficult systems, but suffer from the expensive calculation and storage of a large number of integrals needed to include the second derivatives of the energy with respect to the variational parameters. This limits the application of second-order methods to medium sized molecules. First-order methods require less integrals and therefore show a lower scaling with the system size, but the convergence can be rather slow. We are developing a CASSCF method which provides fast and reliable convergence for large molecules. Our method combines a second-order optimization algorithm of the active orbitals with the first-order super-CI optimization method [4,5] of the inactive orbitals. Furthermore, the coupling with the CI optimization is included by a quasi-Newton method [3]. The resulting CASSCF method provides much faster convergence and through that a lower overall cost than the first-order super-CI method. Also, a lower number of CI evaluations can be achieved through the quasi-Newton convergence acceleration. The convergence and efficiency of the method is demonstrated for several large transition metal complexes.

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