Analytic Gradients for v2RDM-CASSCF methods

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Complete Active Space Self Consistent Field (CASSCF) computations enable an accurate description of the electronic structure in many-electron systems where non-dynamical correlation effects are important. Variational two-electron reduced-density matrix (v2RDM) methods provide one possible route to polynomially-scaling CASSCF computations. Polynomially scaling implementations of CASSCF enable computations on active spaces larger than those for which CASSCF is tractable with configuration-interaction (CI)- driven approaches. v2RDM-driven CASSCF can routinely treat active spaces of 50 electrons in 50 orbitals and the simultaneous optimization of more than 1800 orbitals [1]. Here, we present and benchmark an implementation of analytic electronic energy gradients for v2RDM-driven CASSCF. To validate the implementation of the code, we compared analytic and respective numerical electronic energy gradients at every atomic coordinate of twenty small molecules in several basis sets. We also use our implementation of analytic gradients in the optimization of the geometries of each of the twenty molecules. For this set of molecules, bond lengths from geometry optimization with v2RDM-driven CASSCF are in good agreement with those obtained from (CI)-driven CASSCF. When enforcing two-particle N-representability conditions, v2RDM-CASSCF-optimized bond lengths display a mean unsigned error (MSE) of 0.006 Å, and a maximum unsigned error (MaxUE) of 0.03 Å, when compared to those obtained at the CI-CASSCF level of theory. When enforcing partial three-particle N-representability conditions, the MUE in the bond lengths is reduced to 0.0006 Å, and the MaxUE to only 0.005 Å.

[1] Fosso-Tande, J.; Nguyen, T.-S.; Gidofalvi, G.; DePrince III, A. E.; *Journal of Chemical Theory and Computation,* 2016, *12*, 2260–2271.