Variational optimization of the two-electron reduced-density matrix under pure-state $N$-representability conditions

A. Eugene DePrince III

$^1$ Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390

Abstract

The direct variational optimization of the ground-state two-electron reduced-density matrix (2-RDM) can routinely be achieved via semidefinite programming techniques. The resulting variational 2-RDM (v2RDM) approach can be used to realize polynomially-scaling complete active space self-consistent field (CASSCF) computations applicable to active spaces comprised of as many as 50 electrons in 50 orbitals.$^1$ Such computations are usually performed under ensemble $N$-representability conditions. Accordingly, for degenerate ground states, one has no guarantee that the variationally-obtained 2-RDM represents a pure state. The ensemble nature of the resulting 2-RDMs has important consequences when they are used to extract excited-state information from an extended random phase approximation (ERPA); it has been shown previously that the ERPA fails dramatically in this case, even for simple atomic systems.$^2$ Here, we describe how pure-state $N$-representability conditions can be imposed in the v2RDM procedure.$^3$ 2-RDMs that satisfy both ensemble and pure-state conditions then provide reliable estimates of excitation energies within the ERPA.


$^*$Electronic address: deprince@chem.fsu.edu