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

A. Eugene DePrince III[1]

[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.

[1] J. Fosso-Tande, T.-S. Nguyen, G. Gidofalvi, and A. E. DePrince III, J. Chem. Theory Comput. **12**, 2260 (2016).

[2] H. van Aggelen, B. Verstichel, G. Acke, M. Degroote, P. Bultinck, P. W. Ayers, and D. V. Neck, Comp. and Theor. Chem. **1003**, 50 (2013).

[3] A. E. DePrince III, J. Chem. Phys. **145**, 164109 (2016).

*Electronic address: `deprince@chem.fsu.edu`