

# Rank restriction for the variational calculation of two-electron reduced density matrices of many-electron atoms and molecules

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Variational minimization of the ground-state energy as a function of the two-electron reduced density matrix (2-RDM), constrained by necessary  $N$ -representability conditions, provides a polynomial-scaling approach to studying strongly correlated molecules without computing the many-electron wave function. Here we introduce a route to enhancing necessary conditions for  $N$  representability through rank restriction of the 2-RDM. Rather than adding computationally more expensive  $N$ -representability conditions, we directly enhance the accuracy of two-particle (2-positivity) conditions through rank restriction, which removes degrees of freedom in the 2-RDM that are not sufficiently constrained. We select the rank of the particle-hole 2-RDM by deriving the ranks associated with model wave functions, including both mean-field and antisymmetrized geminal power (AGP) wave functions. Because the 2-positivity conditions are exact for quantum systems with AGP ground states, the rank of the particle-hole 2-RDM from the AGP ansatz provides a minimum for its value in variational 2-RDM calculations of general quantum systems. To implement the rank-restricted conditions, we extend a first-order algorithm for large-scale semidefinite programming. The rank-restricted conditions significantly improve the accuracy of the energies; for example, the percentages of correlation energies recovered for HF, CO, and N<sub>2</sub> improve from 115.2%, 121.7%, and 121.5% without rank restriction to 97.8%, 101.1%, and 100.0% with rank restriction. Similar results are found at both equilibrium and nonequilibrium geometries. While more accurate, the rank-restricted  $N$ -representability conditions are less expensive computationally than the full-rank conditions.

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## I. INTRODUCTION

Significantly more information is encoded within the wave function than is necessary for the calculation of energies and properties of many-electron quantum systems. In 1955 Mayer proposed in *Physical Review* calculating the ground-state energy variationally as a functional of the two-electron reduced density matrix (2-RDM) rather than the  $N$ -electron wave function [1–3]. Unlike the wave function the 2-RDM scales polynomially with the number  $N$  of electrons in the molecule. In further work, however, it became apparent that the 2-RDM must be constrained by nontrivial conditions to ensure that it is representable by an  $N$ -electron density matrix (or wave function), and the search for these conditions became known as the  $N$ -representability problem [2,4–24]. For nearly 50 years the direct calculation of the 2-RDM without the wave function was stymied by the need for better  $N$ -representability conditions and better optimization methods.

The variational computation of an  $N$ -particle system's ground-state energy as a functional of the 2-RDM has recently been realized through advances in (i) developing  $N$ -representability conditions [6,8,9,11,12,22] and (ii) designing optimization algorithms [12–15,25–28]. A systematic hierarchy of  $N$ -representability conditions has been developed in the form of  $p$ -positivity conditions [5,9,11,17], which constrain  $p + 1$  distinct metric matrices of the fermionic  $p$ -RDM to be positive semidefinite. (A matrix is positive semidefinite if and only if its eigenvalues are nonnegative). The  $p + 1$  metric matrices represent the probability distributions of  $p - q$  particles and  $q$  holes with  $q$  ranging from 0 to  $p$

where a hole is the absence of a particle [9]. The  $p$ -positivity conditions ensure that each of these probability distributions is nonnegative. These conditions, even for small  $p$ , are capable of capturing both moderate and strong electron correlation; for example, the 2-positivity conditions are necessary and sufficient for computing the ground-state energies of pairing Hamiltonians [11], often employed in modeling long-range order and superconductivity.

Minimizing the ground-state energy as a 2-RDM functional constrained by these conditions produces a special type of optimization known as semidefinite programming (SDP) [13–15,25–33]. Importantly, because SDP problems are solvable in polynomial time, the variational 2-RDM method provides a polynomial-time relaxation of the exponentially scaling many-electron problem that is suitable for describing strong electron correlation. The 2-RDM methodology has been applied in quantum chemistry and condensed-matter physics to studying many-electron molecules and their reactions [21,23,34,35], quantum phase transitions [36,37], quantum dots [38], molecular clusters [39,40], and spin systems such as the Hubbard [41] and Ising [42] models. While new wave-function methods for strong correlation are being actively developed [43–50], traditional wave-function methods are limited to linear combinations of approximately  $10^9$  molecular configurations.

In this paper we present a new approach to improving the accuracy of energies from the 2-RDM method through rank restriction of the  $N$ -representability conditions. The accuracy of the 2-RDM calculations with 2-positivity can be dramatically enhanced through the addition of 3-positivity conditions [12,17,51,52], but these conditions significantly increase the total computational cost of the calculations. Rather than turning to 3-positivity, we propose to improve 2-positivity

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more directly without an increase in its computational cost. The central idea is that approximate  $N$ -representability conditions like the 2-positivity constraints should be combined with less flexibility in the 2-RDM than more stringent  $N$ -representability conditions like 3-positivity.

One systematic approach to controlling the flexibility of the 2-RDM is to restrict its rank or the rank of one of its metric matrices. We can motivate the selection of the rank by examining the ranks associated with model wave functions, including mean-field [53] and antisymmetrized geminal power (AGP) [2,54–62] wave functions. Importantly, because the 2-positivity conditions yield the exact ground-state energy of any AGP Hamiltonian—that is, a Hamiltonian whose ground state is described by an AGP wave function [2,11]—the AGP 2-RDM provides a lower bound on the optimal rank of the particle-hole form of the 2-RDM. The resulting rank-restricted  $N$ -representability conditions yield significantly improved ground-state energies at a slightly lower computational cost than unrestricted 2-positivity conditions.

After theoretical results are presented in Sec. II, illustrative applications are made in Sec. III to computing ground-state energies for a set of molecules in several basis sets as well as bond stretching of hydrogen fluoride and diatomic nitrogen. Section IV provides a brief discussion and concluding remarks.

## II. THEORY

The energy is expressed as a functional of the 2-RDM in Sec. II A, and the  $N$ -representability constraints, known as 2-positivity conditions [5,9], are reviewed in Sec. II B. In Sec. II C 1 we derive the maximum rank of the particle-hole  ${}^2G$  matrix for two model wave functions, the Hartree-Fock wave function and the AGP wave function. For the AGP wave function the maximum rank for each block of the spin-adapted particle-hole  ${}^2G$  matrix is also derived. Finally, in Sec. II C 2 we extend a large-scale algorithm for SDP [13,26] to support rank restriction.

### A. Energy functional

Because electrons are indistinguishable with pairwise interactions, the energy of any  $N$ -electron quantum system can be expressed as a linear functional of the two-electron reduced Hamiltonian matrix  ${}^2K$  and the 2-RDM [1–3]:

$$E = \sum_{p,q,s,t} {}^2K_{s,t}^{p,q} {}^2D_{s,t}^{p,q}, \quad (1)$$

$$E = \text{Tr}({}^2K {}^2D), \quad (2)$$

where the indices denote spin orbitals  $\phi_p$  in a finite one-electron basis set  $\{\phi_p\}$ . The elements of the two-electron reduced Hamiltonian matrix are

$${}^2K_{s,t}^{p,q} = \frac{1}{N-1} {}^1K_s^p \delta_t^q + {}^2V_{s,t}^{p,q}, \quad (3)$$

where matrices  ${}^1K$  and  ${}^2V$  contain the one- and two-electron integrals, respectively, and the elements of the 2-RDM are

$${}^2D_{s,t}^{p,q} = \langle \Psi | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_t \hat{a}_s | \Psi \rangle, \quad (4)$$

where  $\hat{a}_p^\dagger$  ( $\hat{a}_p$ ) is a creation (annihilation) operator in second quantization that creates (annihilates) an electron in spin orbital  $\phi_p$  and  $\Psi$  represents the  $N$ -electron wave function.

### B. $N$ -representability conditions

Because not every two-electron density matrix is representable by an  $N$ -electron density matrix, the 2-RDM must be constrained by  $N$ -representability conditions [2,4–6,8–24]. A systematic hierarchy of constraints is furnished by the  $p$ -positivity conditions [5,9,11,17]. The 1-positivity conditions, constraining the one-particle  ${}^1D$  and the one-hole  ${}^1Q$  RDMs to be positive semidefinite, correspond to restricting the eigenvalues of the 1-RDM  $n_p$ , known as natural occupation numbers, to lie between zero and one  $n_p \in [0,1]$ , which enforces the Pauli principle. Coleman [2,4] first proved that these relatively simple conditions plus the usual trace, Hermiticity, and antisymmetry constraints in the definition of a density matrix are not only necessary but also sufficient for the 1-RDM to represent an  $N$ -electron density matrix.

The 2-positivity conditions [5,9], providing necessary constraints on the 2-RDM, constrain the following three metric matrices to be positive semidefinite:

$${}^2D \succeq 0, \quad (5)$$

$${}^2Q \succeq 0, \quad (6)$$

$${}^2G \succeq 0, \quad (7)$$

where the metric matrices  ${}^2D$ ,  ${}^2Q$ , and  ${}^2G$  correspond to the probability distributions for two particles, two holes, and one particle and one hole. In second quantization the elements of these matrices are expressible as

$${}^2X_{s,t}^{p,q} = \langle \Psi | {}^X \hat{C}_{p,q} {}^X \hat{C}_{s,t}^\dagger | \Psi \rangle, \quad (8)$$

where

$${}^D \hat{C}_{p,q} = \hat{a}_p^\dagger \hat{a}_q^\dagger, \quad (9)$$

$${}^Q \hat{C}_{p,q} = \hat{a}_p \hat{a}_q, \quad (10)$$

$${}^G \hat{C}_{p,q} = \hat{a}_p^\dagger \hat{a}_q. \quad (11)$$

All three metric matrices contain equivalent information in the sense that rearranging the creation and annihilation operators produces linear mappings between the elements of the three matrices [1,2,11]; particularly, the two-hole RDM  ${}^2Q$  and the particle-hole RDM  ${}^2G$  can be written in terms of the two-particle RDM  ${}^2D$  as follows:

$${}^2Q_{s,t}^{p,q} = 2 {}^2I_{s,t}^{p,q} - 4 {}^1D_s^p \wedge {}^1I_t^q + {}^2D_{s,t}^{p,q} \quad (12)$$

and

$${}^2G_{s,t}^{p,q} = {}^1I_t^q {}^1D_s^p - {}^2D_{s,q}^{p,t}, \quad (13)$$

where  ${}^1I$  and  ${}^2I$  are the one- and two-particle identity matrices and  $\wedge$  denotes the Grassmann wedge product [63,64]. While all three matrices are interconvertible, the nonnegativity of the eigenvalues of one matrix does not imply the nonnegativity of the eigenvalues of the other matrices, and hence, each semidefinite constraint in Eqs. (5), (6), and (7) provides an important  $N$ -representability condition.

### C. Rank restriction

#### 1. Model wave functions

The best-known model wave function is the mean-field wave function introduced by Hartree, Fock, and Slater [53]. In first quantization the  $N$ -electron Hartree-Fock wave function can be expressed as

$$\Psi_{\text{HF}} = \phi_1(1) \wedge \phi_2(2) \wedge \cdots \wedge \phi_N(N), \quad (14)$$

while in second quantization it can be written as

$$|\Psi_{\text{HF}}\rangle = \left( \prod_{i=1}^N \hat{a}_i^\dagger \right) |0\rangle, \quad (15)$$

where  $|0\rangle$  denotes the vacuum state, the state without any electrons. The rank of the particle-hole 2-RDM (or  ${}^2G$ ), whose elements are given in Eq. (8), equals the number of linearly independent  $N$ -electron functions  $|f_{i,j}\rangle$  having the form

$$|f_{i,j}\rangle = \hat{a}_j^\dagger \hat{a}_i |\Psi\rangle. \quad (16)$$

For the Hartree-Fock wave function the set  $\{|f_{i,j}\rangle\}$  contains the wave function  $|\Psi_{\text{HF}}\rangle$  itself as well as  $(r-N)N$  functions from all single excitations of  $|\Psi_{\text{HF}}\rangle$ . Hence the rank of  ${}^2G$  from a Hartree-Fock wave function is  $(r-N)N+1$ . For a wave function to describe a correlated  $N$ -electron system in  $r$  spin orbitals its particle-hole 2-RDM  ${}^2G$  must have a rank strictly larger than  $(r-N)N+1$ .

A flexible model wave function with electron correlation is the AGP wave function [2,54–62], also known as the projected Bardeen, Cooper, and Schrieffer (BCS) wave function, which can be employed to model Cooper pairing in superconductivity. The  $N$ -electron AGP wave function in first quantization can be written as

$$\Psi_{\text{AGP}} = g(1,2) \wedge g(3,4) \wedge \cdots \wedge g(N-1,N), \quad (17)$$

where  $g(1,2)$  is a two-electron function (or geminal), in contrast to the set of one-electron orbitals  $\{\phi_i\}$ . In second quantization we can define the AGP wave function as a projection of the BCS wave function onto the  $N$ -electron space:

$$|\Psi_{\text{AGP}}\rangle = \hat{P}_N \left[ \prod_{i=1}^{r/2} (1 + \gamma_i \hat{a}_{+i}^\dagger \hat{a}_{-i}^\dagger) \right] |0\rangle, \quad (18)$$

where  $|0\rangle$  is the vacuum state and  $\hat{P}_N$  is the projection operator that projects the BCS wave function onto the Hilbert space of  $N$ -electron wave functions. A key feature of the AGP wave function is the special pairing of orbitals [2], which we denote by  $+i$  and  $-i$  for  $i \in [1, r/2]$ . In the study of superconductivity this pairing is employed to model the observed Cooper pairing of the momenta of electrons.

The rank of  ${}^2G$ , again equaling the number of linearly independent  $N$ -electron functions  $|f_{i,j}\rangle$  in Eq. (16), can be determined for AGP from the pairing of orbitals. For AGP the functions  $|f_{i,j}\rangle$  can be divided into two classes [57]:

$$|f_{i,i}^P\rangle = \hat{P}_{i,i} |\Psi_{\text{AGP}}\rangle, \quad (19)$$

$$|f_{i,j}^Q\rangle = \hat{Q}_{i,j} |\Psi_{\text{AGP}}\rangle, \quad (20)$$

where the  $\hat{P}_{i,i}$  are projection operators and  $\hat{Q}_{i,j}$  are operators whose adjoint operators annihilate the AGP wave function, that is,

$$\hat{Q}_{i,j}^\dagger |\Psi_{\text{AGP}}\rangle = 0. \quad (21)$$

Specifically, when the  $\gamma_i$  are not more than doubly degenerate,  $r/2$  linearly independent functions  $|f_{i,i}^P\rangle$  arise from the projectors,

$$\hat{P}_{i,i} = \hat{a}_i^\dagger \hat{a}_i, \quad (22)$$

and  $r(r-2)/2$  linearly independent functions  $|f_{i,j}^Q\rangle$  arise from the  $\hat{Q}_{i,j}$  operators whose adjoints are

$$\hat{Q}_{i,j}^\dagger = \gamma_i \hat{a}_i^\dagger \hat{a}_j - \text{sgn}(ij) \gamma_j \hat{a}_{-j}^\dagger \hat{a}_{-i}, \quad (23)$$

where  $i, j \in [-r/2, r/2] \setminus [0]$  with  $i \neq j$  and  $i \neq -j$ , and  $\text{sgn}(ij)$  returns the sign of the product of  $i$  and  $j$ .

The fact that each of the  $r(r-2)/2$  operators  $\hat{Q}_{i,j}^\dagger$  annihilates the AGP wave function follows from the pairing property of the orbitals [2,57]. From the definition of the AGP wave function in Eq. (18), it can be seen that in each Slater determinant contributing to the AGP wave function both orbitals in a pair, i.e.,  $\phi_{+i}$  and  $\phi_{-i}$ , are either occupied or unoccupied. Furthermore, each pair in the wave function is weighted by a corresponding element of the vector  $\gamma$ . Hence the actions of the operators  $\gamma_i \hat{a}_i^\dagger \hat{a}_j$  and  $\gamma_j \hat{a}_{-j}^\dagger \hat{a}_{-i}$  on the AGP wave function are always equal or opposite in sign, depending on whether the function  $\text{sgn}(i,j)$  is equal to  $+1$  or  $-1$ , which proves the result. The numbers of linearly independent  $|f_{i,i}^P\rangle$  and  $|f_{i,j}^Q\rangle$  will be less than their maximum values of  $r/2$  and  $r(r-2)/2$  if the  $\gamma_i$  where  $\gamma_i = \gamma_{-i}$  are more than doubly degenerate. Such a case occurs when the AGP wave function reduces to the Hartree-Fock wave function and the numbers of linearly independent  $|f_{i,i}^P\rangle$  and  $|f_{i,j}^Q\rangle$  become 1 and  $N(r-N)$ , respectively. Consequently, for an AGP wave function the maximum rank of  ${}^2G$  is  $r(r-2)/2 + r/2$  or  $r(r-1)/2$ .

In electronic calculations, when the expectation value of the  $z$  component of the spin operator  $\langle \hat{S}_z \rangle$  vanishes, the basis functions of the  ${}^2G$  metric matrix can be spin adapted to produce a block diagonal  ${}^2G$  matrix with four blocks [65]. The four blocks correspond to the following four  ${}^G \hat{C}_{\bar{i}, \bar{j}}$  operators:

$${}^G \hat{C}_{\bar{i}, \bar{j}}^{(0,0)} = \frac{1}{\sqrt{2}} (\hat{a}_{i\alpha}^\dagger \hat{a}_{j\alpha} + \hat{a}_{i\beta}^\dagger \hat{a}_{j\beta}), \quad (24)$$

$${}^G \hat{C}_{\bar{i}, \bar{j}}^{(1,-1)} = \hat{a}_{i\beta}^\dagger \hat{a}_{j\alpha}, \quad (25)$$

$${}^G \hat{C}_{\bar{i}, \bar{j}}^{(1,0)} = \frac{1}{\sqrt{2}} (\hat{a}_{i\alpha}^\dagger \hat{a}_{j\alpha} - \hat{a}_{i\beta}^\dagger \hat{a}_{j\beta}), \quad (26)$$

$${}^G \hat{C}_{\bar{i}, \bar{j}}^{(1,+1)} = \hat{a}_{i\alpha}^\dagger \hat{a}_{j\beta}, \quad (27)$$

where the bar above the index refers to the spatial part of the orbital, the spin part of each orbital is denoted as either  $\alpha$  ( $+1/2$ ) or  $\beta$  ( $-1/2$ ), and the upper right indices of  ${}^G \hat{C}_{\bar{i}, \bar{j}}^{(s,m)}$  denote the square of the total spin and the  $z$  component of the total spin for the two-electron operators. If the pairing within the AGP ansatz is taken to be between spin orbitals sharing the same spatial component, the AGP wave function in Eq. (18) can be rewritten with  $\bar{i}\alpha$  and  $\bar{j}\beta$  replacing  $+i$  and  $-i$ .

To determine the rank of the  ${}^2G$  spin blocks, we can spin adapt the projection operators in Eq. (22) and the adjoint of the annihilation operators in Eq. (23), respectively, to obtain

$$\hat{P}_{\bar{i},\bar{i}}^{(0,0)} = \frac{1}{\sqrt{2}}(\hat{P}_{\bar{i}\alpha,\bar{i}\alpha} + \hat{P}_{\bar{i}\beta,\bar{i}\beta}) \quad (28)$$

and

$$\hat{Q}_{\bar{i},\bar{j}}^{(0,0)} = \frac{1}{\sqrt{2}}(\hat{Q}_{\bar{i}\alpha,\bar{j}\alpha} + \hat{Q}_{\bar{i}\beta,\bar{j}\beta}), \quad (29)$$

$$\hat{Q}_{\bar{i},\bar{j}}^{(1,-1)} = \hat{Q}_{\bar{i}\alpha,\bar{j}\beta}, \quad (30)$$

$$\hat{Q}_{\bar{i},\bar{j}}^{(1,0)} = \frac{1}{\sqrt{2}}(\hat{Q}_{\bar{i}\alpha,\bar{j}\alpha} - \hat{Q}_{\bar{i}\beta,\bar{j}\beta}), \quad (31)$$

$$\hat{Q}_{\bar{i},\bar{j}}^{(1,+1)} = \hat{Q}_{\bar{i}\beta,\bar{j}\alpha}. \quad (32)$$

All  $r_s$  spin-adapted projection operators contribute to the (0,0) spin block of  ${}^2G$ , and  $r_s(r_s - 1)/2$   $\hat{Q}$ -type operators contribute to each of the (0,0), (1,-1), (1,0), and (1,+1) spin blocks where the number  $r_s$  of spatial orbitals equals one-half the number  $r$  of spin orbitals. Hence the rank of the singlet spin block (0,0) of  ${}^2G$  is  $r_s(r_s + 1)/2$ , and the ranks of the three triplet spin blocks of  ${}^2G$  are  $r_s(r_s - 1)/2$ . When  $\langle \hat{S}_z \rangle = 0$ , all three triplet blocks are identical [65].

## 2. Semidefinite programming

The variational 2-RDM method with 2-positivity conditions minimizes the ground-state energy as a 2-RDM functional,

$$\text{minimize } E(x) = c^T x, \quad (33)$$

where the vector  $c$  contains information about the quantum system in the form of the two-electron reduced Hamiltonian in Eq. (3) [9] and the vector  $x$  contains the three different metric-matrix forms of the 2-RDM whose elements are given in Eq. (8). Because the three metric matrices in  $x$  are interrelated by linear mappings,

$$Ax = b, \quad (34)$$

and constrained to be positive semidefinite,

$$M(x) = \begin{pmatrix} {}^2D & 0 & 0 \\ 0 & {}^2Q & 0 \\ 0 & 0 & {}^2G \end{pmatrix} \geq 0, \quad (35)$$

where the operator  $M$  maps the vector  $x$  to a matrix, the energy minimization constitutes a special type of constrained optimization known as semidefinite programming (SDP) [13–15,25–33]. SDP is a generalization of linear programming from linear scalar inequalities to linear matrix inequalities.

Second-order algorithms for SDP, developed in the 1990s [30,31], have an expensive  $r^{16}$  scaling [10,11] in floating-point operations when applied to variational 2-RDM calculations with 2-positivity constraints. Zhao *et al.* [12] introduced a dual formulation of the 2-RDM optimization that decreased the computational scaling to  $r^{12}$ , and one of the authors developed two first-order algorithms, a matrix-factorization method [13,14,26], and a boundary-point method [28] that reduce the floating-point operations to  $r^6$  and the memory requirements from  $r^8$  to  $r^4$ . Cancés *et al.* [15], who studied a

dual formulation of the SDP problem, confirmed the efficiency of the matrix factorization method, and Verstichel *et al.* [22] introduced a first-order algorithm based on interior-point methods.

For the rank-restricted  $N$ -representability conditions the SDP optimization must be modified to include rank restriction of the particle-hole  ${}^2G$  metric matrix within  $M$ . In the matrix-factorization method the solution matrix  $M$  is explicitly constrained to be positive semidefinite by a matrix factorization [13,14,26]:

$$M = RR^*. \quad (36)$$

Importantly, the rank of  $M$  or any of its sub-blocks can be readily constrained to an integer  $q$  by restricting the number of columns of  $R$  to  $q$  where  $q$  is less than the dimension of the square matrix  $M$ . With this flexibility we can solve SDP problems both with and without rank restriction. If the rank of a block in  $R$  is restricted to an unphysical value such as an integer less than the rank corresponding to a Hartree-Fock model wave function, the algorithm generally will not converge. Otherwise, convergence of the rank-restricted SDP is similar to that of the unrestricted SDP.

## III. APPLICATIONS

After an overview of computational details and a summary of  $N$ -representability conditions, we present results of the rank-restricted variational 2-RDM method for molecules at both equilibrium and nonequilibrium geometries.

### A. Computational details

The variational 2-RDM method with 2-positivity and rank-restricted 2-positivity conditions is illustrated with calculations on several molecules at equilibrium and nonequilibrium geometries in minimal Slater-type orbital (STO-6G) [66], double- $\zeta$  (DZ) [67], and correlation-consistent polarized double- $\zeta$  (cc-pVDZ) [68] basis sets. Nonequilibrium geometries are obtained from the *Handbook of Chemistry and Physics* [69], all core orbitals are double occupied (frozen), and the molecules are in singlet states. The calculation of one- and two-electron integrals and full configuration interaction (FCI) is implemented in the quantum chemistry package GAMESS (USA) [70].

### B. Summary of $N$ -representability conditions

Variational RDM ground-state energies are computed with the first-order nonlinear SDP algorithm developed by Mazzotti [13,14,26]. The following  $N$ -representability conditions are enforced:

(1) Hermiticity of the 2-RDM:

$${}^2D_{k,l}^{i,j} = {}^2D_{i,j}^{k,l}. \quad (37)$$

(2) Antisymmetry of upper and lower indices,

$${}^2D_{k,l}^{i,j} = -{}^2D_{k,l}^{j,i} = -{}^2D_{l,k}^{i,j} = {}^2D_{l,k}^{j,i}, \quad (38)$$

is enforced by antisymmetrized basis functions  $\tilde{\phi}_{i,j} = 1/\sqrt{2}(\phi_{i,j} - \phi_{j,i})$ .



TABLE I. The percentage of the correlation energy recovered by the variational 2-RDM method with full-rank and rank-restricted  $N$ -representability conditions is shown for the molecules CO, N<sub>2</sub>, H<sub>2</sub>O, HF, and NO<sup>+</sup> in a variety of basis sets.

Molecule	Basis set	Full rank	Theoretical rank	Full CI energy (a.u.)	Correlation energy (a.u.)	% Correlation energy	
						Full rank	Theoretical rank
CO	STO-6G	64	36	-112.443174	-0.139676	108.5	101.2
	DZ	256	136	-112.893590	-0.208672	119.3	102.5
	cc-pVDZ	676	351	-113.054884	-0.305767	121.7	101.1
N <sub>2</sub>	STO-6G	64	36	-108.699813	-0.158189	107.6	97.7
	DZ	256	136	-109.104172	-0.226029	119.1	102.8
	cc-pVDZ	676	351	-109.278339	-0.329000	121.5	100.0
H <sub>2</sub> O	STO-6G	36	21	-75.728838	-0.050041	104.0	101.7
	DZ	144	78	-76.141153	-0.132021	111.8	102.9
	cc-pVDZ	529	276	-76.241677	-0.214915	116.7	107.3
HF	STO-6G	36	21	-99.526353	-0.026196	100.0	99.7
	DZ	100	55	-100.146049	-0.124147	107.2	100.5
	cc-pVDZ	324	171	-100.228652	-0.209363	115.2	97.8
NO <sup>+</sup>	STO-6G	64	36	-128.637594	-0.241971	108.7	102.4
	DZ	256	136	-129.060275	-0.315068	115.3	103.6

(3) Trace conditions on the spin-adapted blocks of the 2-RDM [65]:

$$\begin{aligned}\text{Tr}({}^2D^{(1,0)}) &= N_s(N_s - 1), \\ \text{Tr}({}^2D^{(0,0)}) &= N_s(N_s + 1),\end{aligned}\quad (39)$$

where  $N_s = N/2$ .

(4) Contraction of the spin-adapted 2-RDM [65] onto the 1-RDM:

$$\begin{aligned}(N_s - 1) {}^1D_{j\alpha}^{i\alpha} &= \sum_k {}^2D_{i,k;j,k}^{(1,1)}, \\ (N_s + 1) {}^1D_{j\alpha}^{i\alpha} &= \sum_k {}^2D_{i,k;j,k}^{(0,0)}.\end{aligned}\quad (40)$$

(5) The 2-positivity conditions [Eqs. (5)–(7)], on three different representations of the 2-RDM whose elements, given in Eq. (8), are related by the linear mappings in Eqs. (12) and (13).

(6) In the case of rank restriction, the rank of the particle-hole matrix  ${}^2G^{(0,0)}$  is restricted.

### C. Results

Two sets of  $N$ -representability constraints are imposed in the calculations shown in Tables I, II, and III and Figs. 1 and 2: (i) 2-positivity conditions without rank restriction, labeled full rank; and (ii) 2-positivity conditions plus rank restriction, labeled theoretical rank, in which the rank of the  ${}^2G^{(0,0)}$  block of the particle-hole matrix is restricted to  $r_s(r_s + 1)/2$ —its maximum value from a model AGP wave function.

For a variety of molecules and basis sets Table I shows the percentage of the correlation energy recovered by the variational 2-RDM method with full-rank and rank-restricted  $N$ -representability conditions. Rank restriction significantly improves the percentage of correlation energy for all molecules and basis sets. For CO the 2-positivity conditions *without* restriction yield 108.5%, 119.3%, and 121.7% of the correlation

energy in STO-6G, DZ, and cc-pVDZ basis sets, while these conditions *with* rank restriction yield 101.2%, 102.5%, and 101.1% of the correlation energy. Even though the theoretical rank increases dramatically with basis-set size, the percentage of the correlation energy recovered remains nearly constant. Because the rank restriction limits the flexibility of the 2-RDM, we observe that the computed energies with rank restriction are neither consistently above nor below the FCI energy.

Dissociation of the triple-bonded nitrogen molecule N<sub>2</sub> provides a classic case of strong electron correlation. Table II and Fig. 1 present the potential energy curve of N<sub>2</sub> in the cc-pVDZ basis set from the variational 2-RDM method with and without rank restriction. At  $R = 1.485$  Å, while the 2-RDM method with the full rank recovers 119.6% of the correlation energy, the 2-RDM method with the theoretical rank yields 99.6% of the correlation energy. At this distance

TABLE II. The percentage of correlation energy along the potential energy curve of the nitrogen molecule N<sub>2</sub> in the cc-pVDZ basis set is reported from the variational 2-RDM method with and without rank restriction. At  $R = 1.485$  Å in a region of the potential energy curve where the spins are recoupling, sometimes known as the spin recoupling region, the error from the rank-restricted 2-RDM method is only +0.002 a.u. relative to FCI.

Bond length (Å)	Full CI energy (a.u.)	Correlation energy (a.u.)	% Correlation energy	
			Full rank	Theoretical rank
0.80	-108.664476	-0.257118	120.7	97.5
1.1208	-109.282139	-0.332762	120.1	98.7
1.175	-109.275424	-0.347604	120.1	98.7
1.475	-109.141160	-0.442743	119.6	99.6
1.85	-109.008801	-0.590167	116.4	97.5
2.225	-108.970662	-0.748815	111.3	96.2
2.6	-108.963937	-0.874616	108.2	95.5
2.975	-108.962249	-0.963251	106.8	95.4

TABLE III. The percentage of correlation energy along the potential energy curve of hydrogen fluoride in the cc-pVDZ basis set is reported from the variational 2-RDM method with and without rank restriction. At  $R = 1.95 \text{ \AA}$  in the spin-recoupling region the rank restriction reduces the error from  $-44.5 \text{ a.u.}$  to  $-3.1 \text{ a.u.}$

Bond length ( $\text{\AA}$ )	Full CI energy (a.u.)	Correlation energy (a.u.)	% Correlation energy	
			Full rank	Theoretical rank
0.70	-100.129860	-0.199411	115.3	96.1
0.9161	-100.228633	-0.209189	115.2	97.6
1.2	-100.181953	-0.222427	115.3	98.0
1.3	-100.157836	-0.227830	115.3	98.3
1.5	-100.113798	-0.240945	115.5	97.2
1.95	-100.052917	-0.283544	115.7	101.1
2.8	-100.026420	-0.369590	115.6	104.7

in a region of the potential energy curve where the spins are recoupling, sometimes known as the spin recoupling region, the error from the rank-restricted 2-RDM method is only  $+0.002 \text{ a.u.}$  relative to FCI. Figure 1 shows that the potential energy curve from the rank-restricted 2-RDM method closely agrees with the curve from FCI in a large region surrounding the equilibrium geometry. The largest errors from rank restriction occur at significantly stretched geometries, where strong spin entanglement increases the actual rank of the particle-hole  ${}^2G$  matrix. In contrast, as observed in previous work, the 2-RDM method without rank restriction has its largest errors in the spin-recoupling region of the potential

energy curve. One measure for the potential curve's shape is the nonparallelity error, the difference between the largest error and the smaller error along the curve relative to FCI. While the 2-RDM methods with and without rank restriction have similar nonparallelity errors over the whole curve shown in Fig. 1, in the region  $R \in [0.8, 1.85]$  the rank restriction improves the nonparallelity error from  $0.044 \text{ a.u.}$  to  $0.013 \text{ a.u.}$

Due to the high electronegativity of fluorine, the dissociation of the hydrogen fluoride molecule illustrates the breaking of a polar covalent single bond. Table III and Fig. 2 present the potential energy curve of HF in the cc-pVDZ basis set from the variational 2-RDM method with and without rank restriction.

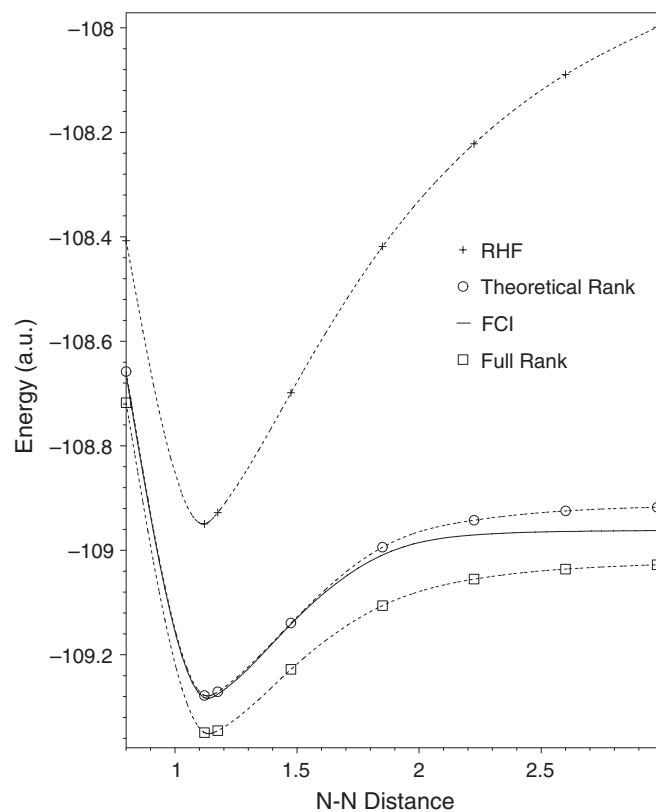


FIG. 1. The potential energy curve of the nitrogen molecule  $\text{N}_2$  in the cc-pVDZ basis set from the variational 2-RDM method with and without rank restriction. Results are compared with those from Hartree-Fock and FCI.

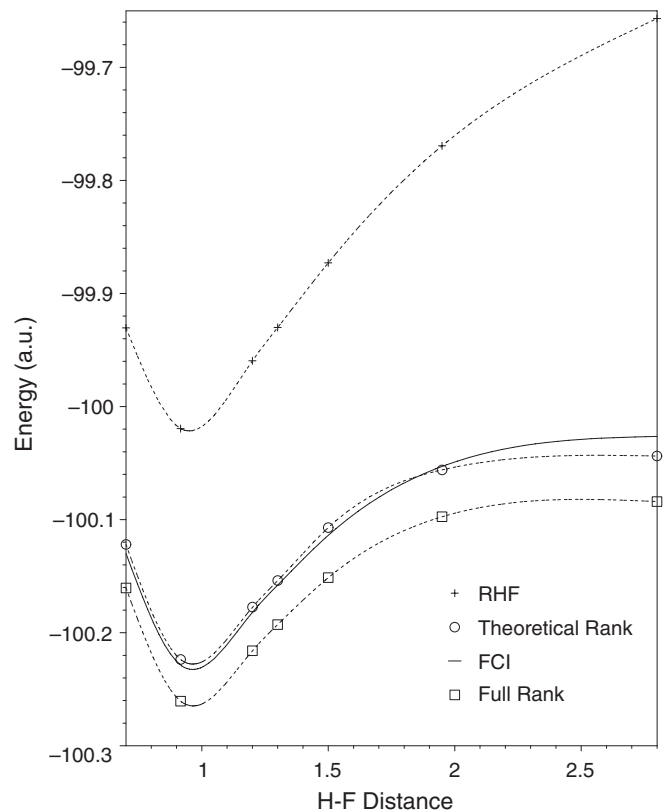


FIG. 2. The potential energy curve of the hydrogen fluoride molecule in the cc-pVDZ basis set from the variational 2-RDM method with and without rank restriction. Results are compared with those from Hartree-Fock and FCI.

At all bond lengths the rank restriction significantly reduces the error in the percentage of the correlation energy relative to FCI. At  $R = 1.95$  in the spin-recoupling region the rank restriction reduces the error from  $-44.5$  a.u. to  $-3.1$  a.u. In the region  $R \in [0.7, 2.8]$  shown in Fig. 2 the rank restriction decreases the nonparallelity error from  $0.027$  a.u. to  $0.024$  a.u., and in the region  $R \in [0.7, 1.95]$  it decreases the nonparallelity error from  $0.014$  a.u. to  $0.010$  a.u. In contrast to the triple-bonded  $N_2$ , the singly bonded hydrogen fluoride at highly stretched geometries has energies from the rank restriction below those from FCI.

#### IV. DISCUSSION AND CONCLUSIONS

Variational minimization of the ground-state energy as a function of the 2-RDM [9–24], constrained by  $N$ -representability conditions, provides a polynomial-scaling approach to studying strongly correlated molecules without computing the many-electron wave function. Here we have introduced a new approach to enhancing necessary conditions for  $N$ -representability through rank restriction of the 2-RDM. Applications were made to molecules at both equilibrium and nonequilibrium geometries.

An important set of  $N$ -representability conditions on the 2-RDM is the 2-positivity conditions, which restrict the probability distributions of two particles ( ${}^2D$ ), two holes ( ${}^2Q$ ), and a particle-hole pair ( ${}^2G$ ) to be nonnegative. In Sec. II C 1 we derived the maximum rank of the particle-hole  ${}^2G$  metric matrix for two model wave functions, the Hartree-Fock and the AGP wave functions. The Hartree-Fock wave functions are a small subset of the AGP wave functions, and hence their particle-hole matrices have a maximum rank  $(r - N)N + 1$  which is strictly less than the maximum rank  $r(r - 1)/2$  of the AGP particle-hole matrices. Because the 2-positivity conditions constrain AGP Hamiltonians—that is, Hamiltonians with AGP ground-state wave functions—to yield the exact ground-state energies, the rank of the AGP  ${}^2G$  matrix provides a minimum rank for the molecular particle-hole  ${}^2G$  matrix within variational 2-RDM calculations of general systems. Selecting a smaller rank for  ${}^2G$  would render the variational 2-RDM method inexact for

AGP Hamiltonians. Unlike the case in Hartree-Fock theory, the maximum rank of  ${}^2G$  within the AGP ansatz is independent of the number  $N$  of particles, which reflects its independence from a reference determinant wave function and hence, its ability to treat strong electron correlation.

The variational 2-RDM method with rank-restricted 2-positivity conditions was applied to computing the energies and 2-RDMs for a variety of molecules at equilibrium geometries as well the potential energy curves of the nitrogen and hydrogen fluoride molecules. Specifically, the rank of the singlet spin block of the particle-hole matrix was restricted to its maximum value from an AGP wave function  $r_s(r_s + 1)/2$  with  $r_s = r/2$ . The rank-restricted conditions were implemented through an extension of the first-order matrix-factorization algorithm for large-scale SDP. The results demonstrate that rank restriction significantly improves the accuracy of computed energies. For example, the percentages of correlation energies recovered for HF, CO, and  $N_2$  improve from 115.2%, 121.7%, and 121.5% without rank restriction to 97.8%, 101.1%, and 100.0% with rank restriction, respectively. The improvement occurs at equilibrium and nonequilibrium geometries and across basis sets. Computationally, the rank-restricted conditions are slightly less expensive than the full 2-positivity conditions. Rank restriction removes degrees of freedom that are not sufficiently constrained by the 2-positivity conditions without sacrificing the method's ability to treat strong electron correlation, as seen in the bond dissociation of  $N_2$ . Although further research is needed to study the method in larger molecules such as polyaromatic hydrocarbons [21,35] and firefly luciferin [23], the present results indicate that rank restriction is a promising approach to improving the 2-positivity conditions within the variational 2-RDM method without increasing computational cost.

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