

Variational Two-electron Reduced Density Matrix Theory for Many-electron Atoms and Molecules: Implementation of the Spin- and Symmetry-adapted T_2 Condition through First-order Semidefinite Programming

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Abstract

The energy and properties of a many-electron atom or molecule may be directly computed from a variational optimization of a two-electron reduced density matrix (2-RDM) that is constrained to represent many-electron quantum systems. In this paper we implement a variational 2-RDM method with a representability constraint, known as the T_2 condition. The optimization of the 2-RDM is performed with a first-order algorithm for semidefinite programming [Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004)] which, because of its lower computational cost in comparison to second-order methods, allows the treatment of larger basis sets. We also derive and implement a spin- and symmetry-adapted formulation of the T_2 condition that significantly decreases the size of the largest block in the T_2 matrix. The T_2 condition, originally derived by Erdahl [Int. J. Quantum Chem. **13**, 697 (1978)], was recently applied via a second-order algorithm to atoms and molecules [Zhao et al., J. Chem. Phys. **120**, 2095 (2004)]. While these calculations were restricted to molecules at equilibrium geometries in minimal basis sets, we apply the 2-RDM method with the T_2 condition to compute the electronic energies of molecules in both minimal and non-minimal basis sets at equilibrium as well as non-equilibrium geometries. Accurate potential energies curves are produced for BH, HF, and N₂. Results are compared with the 2-RDM method without the T_2 condition as well as several wavefunction methods.

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I. INTRODUCTION

In 1959 Charles Coulson recognized the potential benefits of describing the electronic energies and properties of atoms and molecules by the two-electron reduced density matrix (2-RDM) rather than the many-electron wavefunction [1]. As Coulson was aware, however, representing the wavefunction by a 2-RDM is challenging. Not every two-electron density matrix derives from the integration of an N -electron density matrix or wavefunction, and hence, it is necessary to constrain the set of two-electron density matrices to ensure that each member is representable by an N -electron wavefunction [2]. Coleman referred to these constraints as *N -representability* conditions, and the search for these constraints became known as the *N -representability problem* [3–6].

A direct *non-variational* calculation of the 2-RDM without the many-electron wavefunction was realized in the 1990s through the solution of the contracted Schrödinger equation [7–18]. More recently, Nakata et al. and Mazziotti employed advances in optimization to implement a *variational* calculation of the 2-RDM without computation of the many-electron wavefunction or approximation of higher RDMs [19–24]. These calculations minimize the energy with a 2-RDM constrained by approximate *N -representability* conditions through a generalization of linear programming known as semidefinite programming [25]. In this method ground-state energies are computable with an accuracy that is consistent at both equilibrium and non-equilibrium geometries. While 2-RDM computations in the 1970s had treated four-electron atoms and molecules like Be, C^{+2} , and He_2 [26–28], systematic calculations of larger systems required better algorithms for semidefinite programming. Recently, Mazziotti developed a *first-order*, nonlinear algorithm for solving the semidefinite program of the 2-RDM method whose memory and floating-point requirements are lower by orders of magnitude than those of the *second-order* algorithms [29, 30]. The first-order methods only require evaluation of the first derivatives (gradient) while the second-order methods utilize both first and second derivatives (Hessian). Application of this algorithm has been made to larger molecules and basis sets [29–32].

The variational 2-RDM calculations of Nakata et al. [19, 21] and Mazziotti [20, 22] employ a set of *N -representability* conditions, known as 2-positivity conditions, which constrain three different forms of the 2-RDM to be positive semidefinite. These conditions appeared in the work of Coleman [4] and Garrod and Percus [33]. In 1998 Mazziotti examined solving

the contracted Schrödinger equation while constraining the 4-RDM to be positive semidefinite [12]. This and other work on the contracted Schrödinger equation [7–18] highlighted the importance of the 3- and 4-RDMs in the computation of the 2-RDM. Erdahl and Jin [34] and Mazziotti and Erdahl [35] extended the 2-positivity conditions to p -positivity conditions that constrain $p + 1$ forms of the p -RDM to be positive semidefinite. Calculations on spin systems show that the 3-positivity conditions provide highly accurate ground-state energies for both weakly and highly correlated scenarios [35, 36]. Because 3-positivity conditions are relatively expensive for atoms and molecules, two different sets of *partial 3-positivity conditions* have been proposed: (i) the lifting conditions [20, 36], and (ii) the T_1 and T_2 conditions [5, 37]. The T_1 and T_2 conditions, proposed by Erdahl [5], have recently been implemented by Zhao et al. [37] for atoms and molecules in minimal basis sets.

In the present paper we implement the T_2 condition within the first-order, nonlinear algorithm for semidefinite programming to explore the accuracy of this partial 3-positivity condition for molecules in minimal and non-minimal basis sets at both equilibrium and stretched geometries. The efficiency of the variational 2-RDM method with both 2-positivity and T_2 conditions is enhanced by adapting the basis set to account for spin and spatial symmetries. The spin and symmetry adaptation of the basis set generates smaller matrices to be constrained positive semidefinite. Application of the method is made to a variety of molecules at equilibrium and non-equilibrium geometries as well as the potential energy curves of BH, HF, and N_2 . The present calculations confirm the accuracy reported by Zhao et al. [37] for minimal basis sets while demonstrating that these N -representability conditions remain accurate at stretched geometries and in larger basis sets.

II. THEORY

After expressing the energy as a functional of the 2-RDM, we discuss an important set of N -representability constraints, known as the positivity conditions, especially the 2- and 3-positivity conditions as well as the partial 3-positivity condition T_2 . We explain why the T_2 condition depends only on the 2-RDM through the cumulant expansions of the 3-particle and 3-holes RDMs. The positivity conditions are spin- and symmetry-adapted to make their implementation more computationally efficient.

A. Energy expression

Because the electrons interact pairwise, the many-electron Hamiltonians for all atoms and molecules may be written as

$$\hat{H} = \sum_{i,j,k,l} {}^2K_{k,l}^{i,j} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k, \quad (1)$$

where \hat{a}^\dagger and \hat{a} are the second-quantized creation and annihilation operators, the indices refer to the spin-orbital basis set, and the symbol 2K denotes the two-electron reduced Hamiltonian matrix, containing the one- and two-electron integrals as well as the number N of electrons [12]. The expectation value of the Hamiltonian operator generates the many-electron energy

$$E = \sum_{i,j,k,l} {}^2K_{k,l}^{i,j} {}^2D_{k,l}^{i,j} \quad (2)$$

$$E = \text{Tr}({}^2K {}^2D) \quad (3)$$

as a functional of the reduced Hamiltonian matrix and the two-electron reduced density matrix (2-RDM) where

$${}^2D_{k,l}^{i,j} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | \Psi \rangle. \quad (4)$$

From a knowledge of the 2-RDM any two-electron properties of an atom or molecule may be computed [38].

There are four requirements for a particle matrix to be a fermionic density matrix [4]: the matrix must be (i) normalized to conserve particle number, (ii) Hermitian, (iii) antisymmetric under particle exchange, and (iv) positive semidefinite to keep probabilities nonnegative (A matrix is *positive semidefinite* if and only if all of its eigenvalues are nonnegative). Minimizing the ground-state energy in Eq. (2) with the 2-RDM subject to these conditions, however, produces energies that are significantly below the exact energy within the spin-orbital basis set. The problem is that not every 2-particle density matrix, satisfying these conditions, derives from the integration of an N -electron density matrix (or wavefunction). This set of conditions enforces that a particle matrix is a density matrix but not necessarily a *reduced* density matrix. To perform a realistic variational calculation on the space of two electrons, we must further constraint the 2-RDM to derive from integrating an N -electron density matrix. These additional constraints are known as N -representability conditions.

B. Positivity conditions

With any set of operators \hat{C}_i we can generate from the ground-state wavefunction $|\Psi\rangle$ a set of basis functions

$$\langle\Phi_i| = \langle\Psi|\hat{C}_i \quad (5)$$

for which the metric (or overlap) matrix M with elements

$$M_j^i = \langle\Phi_i|\Phi_j\rangle = \langle\Psi|\hat{C}_i\hat{C}_j^\dagger|\Psi\rangle \quad (6)$$

must be positive semidefinite. We indicate that a matrix has this property by the notation $M \geq 0$. For an RDM which corresponds to a wavefunction these vector-space restrictions are *always* satisfied. More generally, however, these conditions, known as *p-positivity conditions*, offer a systematic approach for imposing N -representability conditions on an RDM *without* using the wavefunction.

1. 1- and 2-positivity conditions

If we choose for each \hat{C}_i a second-quantized operator \hat{a}_i^\dagger which creates a particle in the i^{th} orbital, we determine that the 1-particle reduced density matrix (1-RDM) with matrix elements

$${}^1D_j^i = \langle\Psi|\hat{a}_i^\dagger\hat{a}_j|\Psi\rangle \quad (7)$$

must be positive semidefinite and if we choose for each \hat{C}_i an operator \hat{a}_i which annihilates a particle in the i^{th} orbital, we discover that the 1-hole reduced density matrix (1-HRDM) with matrix elements

$${}^1Q_j^i = \langle\Psi|\hat{a}_i\hat{a}_j^\dagger|\Psi\rangle \quad (8)$$

must also be positive semi-definite. The second-quantized operators may be rearranged according to the anticommutation relation for *fermions*

$$\hat{a}_j\hat{a}_i^\dagger + \hat{a}_i^\dagger\hat{a}_j = \delta_j^i. \quad (9)$$

The relation in Eq. (9) provides a linear mapping between the matrix elements of 1D and 1Q . The 1D and the 1Q conditions have sufficient strength to force the eigenvalues of both 1D and 1Q to lie between 0 and 1. By adding the condition that 1D traces to N , we obtain

Coleman's N -representability conditions for the fermionic 1-RDM [3, 4]. We describe any 1-RDM satisfying these conditions as *1-positive*.

Consider \hat{C} to be a product of two fundamental second-quantized operators. The resulting basis functions in Eq. (5) may be naturally grouped into three orthogonal vector spaces according to the number of creation operators in \hat{C} : (i) $\hat{C} \in \{\hat{a}_i^\dagger \hat{a}_j^\dagger\}$, (ii) $\hat{C} \in \{\hat{a}_i \hat{a}_j\}$, and (iii) $\hat{C} \in \{\hat{a}_i^\dagger \hat{a}_j\}$. For these three spaces the metric matrices M that should be constrained to be positive semidefinite are:

$${}^2D_{p,q}^{i,j} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_q \hat{a}_p | \Psi \rangle, \quad (10)$$

$${}^2Q_{p,q}^{i,j} = \langle \Psi | \hat{a}_i \hat{a}_j \hat{a}_q^\dagger \hat{a}_p^\dagger | \Psi \rangle, \quad (11)$$

$${}^2G_{p,q}^{i,j} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j \hat{a}_q^\dagger \hat{a}_p | \Psi \rangle. \quad (12)$$

These matrices, 2D , 2G , and 2Q , are *linearly* related by rearranging the creation and annihilation operators according to the anticommutation relation in Eq. (9). We describe any 2-RDM satisfying all of these conditions as *2-positive*. Because the contraction of the matrices 2D and 2Q produces positive semidefinite matrices 1D and 1Q respectively, the 2-positivity conditions imply the 1-positivity conditions.

2. p -positivity conditions

The conditions that a p -RDM be p -positive follow from writing the \hat{C}_i in Eq. (5) as products of p second-quantized operators [34, 35]. As in the 2-particle case the resulting basis functions lie in $p+1$ vector spaces according to the number of creation operators in the product. Basis functions between these vector spaces are orthogonal because they represent different numbers of particles. Each metric matrix from one of the $p+1$ vector spaces must be positive semidefinite [20]. Furthermore, all of the metric matrices are connected with each other by the anticommutation relation in Eq. (9). A p -RDM which is p -positive contracts to a $(p-1)$ -RDM which is $(p-1)$ -positive. The four metric matrices for 3-positivity [35] that must be constrained to be positive semidefinite are given by

$${}^3D_{p,q,r}^{i,j,k} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_r \hat{a}_q \hat{a}_p | \Psi \rangle \quad (13)$$

$${}^3E_{p,q,r}^{i,j,k} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_r \hat{a}_q \hat{a}_p | \Psi \rangle \quad (14)$$

$${}^3F_{p,q,r}^{i,j,k} = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j \hat{a}_k \hat{a}_r \hat{a}_q^\dagger \hat{a}_p | \Psi \rangle \quad (15)$$

$${}^3Q_{p,q,r}^{i,j,k} = \langle \Psi | \hat{a}_i \hat{a}_j \hat{a}_k \hat{a}_r \hat{a}_q^\dagger \hat{a}_p^\dagger | \Psi \rangle. \quad (16)$$

We say that a 2-RDM is 3-positive if it arises from the *contraction* of a 3-positive 3-RDM. The conditions for 3-positivity have been examined in variational calculations of spin systems in the work of Erdahl and Jin [34], Mazziotti and Erdahl [35], and Hammond and Mazziotti [36] where they give highly accurate energies and 2-RDMs.

3. Partial 3-positivity conditions

Two different *partial 3-positivity* conditions have been proposed: (i) the lifting conditions of Mazziotti [20, 36], and (ii) the T_1/T_2 conditions of Erdahl [5] implemented by Zhao et al. [37]. Here we focus exclusively on the second class of conditions. Because the addition of any two positive semidefinite matrices produces a positive semidefinite matrix, the four 3-positivity conditions [35] imply the following two weaker conditions:

$$T_1 = {}^3D + {}^3Q \geq 0 \quad (17)$$

$$T_2 = {}^3E + {}^3F \geq 0, \quad (18)$$

known as the T_1 and T_2 conditions [5, 37]. For fermions the T_1 and T_2 matrices have the interesting property that they may be exactly evaluated from a knowledge of the 2-RDM. To see this for T_1 , we recall the cumulant expansion [17, 39–43] for the 3-particle and 3-hole RDMs

$${}^3D/6 = {}^1D \wedge {}^1D \wedge {}^1D + 3({}^2D/2 - {}^1D \wedge {}^1D) \wedge {}^1D + {}^3\Delta \quad (19)$$

and

$${}^3Q/6 = {}^1Q \wedge {}^1Q \wedge {}^1Q + 3({}^2Q/2 - {}^1Q \wedge {}^1Q) \wedge {}^1Q - {}^3\Delta, \quad (20)$$

where the wedge \wedge denotes the antisymmetric tensor product, known as the Grassmann wedge product [12, 44], and the symbol ${}^3\Delta$ represents the *connected (or cumulant)* portion of the 3-RDM which cannot be expressed as wedge products of the lower RDMs. Upon addition of the 3-particle and the 3-hole RDMs to form T_1 , the connected 3-RDMs ${}^3\Delta$ exactly cancel, and hence, the T_1 matrix depends only upon the 2-particle RDM. Using that the expectation value of Eq. (9) yields the matrix equation

$${}^1Q + {}^1D = {}^1I \quad (21)$$

with 1I denoting the one-particle identity matrix, the T_1 matrix (or the sum of Eqns. (19) and (20)) may be written as a *linear* functional of the 2-RDM

$$T_1/6 = {}^1I \wedge {}^1I \wedge {}^1I - 3 {}^1D \wedge {}^1I \wedge {}^1I + 3 {}^2D/2 \wedge {}^1I. \quad (22)$$

Similarly, because the elements of the T_2 matrix can be expressed as

$$(T_2)_{l,m,n}^{i,j,k} = ({}^2D_{l,m}^{i,j} + {}^2Q_{i,j}^{l,m}) \delta_n^k - (T_1)_{l,m,k}^{i,j,n}, \quad (23)$$

it follows that the connected parts of the 3-RDM again cancel.

4. Spin- and symmetry-adaptation

For electronic systems each basis set index represents both spatial and spin information where the spin quantum number σ , either $\alpha(+1/2)$ or $\beta(-1/2)$, denotes the eigenvalue of the spin-orbital for the spin angular momentum operator along the z-axis \hat{S}_z . When the Hamiltonian for the quantum system is spin independent, only blocks of the Hamiltonian matrix between basis functions with the same spin quantum numbers for both the square of the total spin angular momentum operator \hat{S}^2 and the operator \hat{S}_z are non-vanishing. Modifying basis functions of the many-body Hamiltonian to be eigenfunctions of \hat{S}^2 and \hat{S}_z is known as *spin adaptation*. The spin-adapted 1-RDM has the following block structure

$${}^1D = \begin{pmatrix} {}^1D_\alpha^\alpha & 0 \\ 0 & {}^1D_\beta^\beta \end{pmatrix}. \quad (24)$$

For the 2-RDM only the spin structure associated with \hat{S}_z has been considered in variational density-matrix calculations [19, 20, 22, 24, 37]. If only \hat{S}_z is considered, the 2-RDM, where we build the antisymmetry of the fermions into the matrix, has the spin structure

$${}^2D = \begin{pmatrix} {}^2D_{\alpha,\alpha}^{\alpha,\alpha} & 0 & 0 \\ 0 & {}^2D_{\alpha,\beta}^{\alpha,\beta} & 0 \\ 0 & 0 & {}^2D_{\beta,\beta}^{\beta,\beta} \end{pmatrix}. \quad (25)$$

If r_s denotes the number of orbitals, then the dimensions of the $\alpha\alpha$ - and the $\alpha\beta$ -blocks of the 2-RDM are $r_s(r_s - 1)/2$ and r_s^2 respectively. Each of these 2-RDM blocks contract to the 1-RDM blocks. Specifically, the $\alpha\alpha$ - and the $\beta\beta$ -blocks of the 2-RDM contribute by contraction to the α - and β -blocks of the 1-RDM respectively while the $\alpha\beta$ -block of the

2-RDM contributes to the α -block of the 1-RDM upon contraction of the β indices and the β -block of the 1-RDM upon contraction of the α indices. In the case of a closed-shell atom or molecule where the α and the β spins are indistinguishable, the two blocks of the 1-RDM are the same, and the first and the last blocks of the 2-RDM are also equal.

Both the 1- and the 2-hole RDMs have the same spin structure as the 1- and the 2-particle RDMs. The 2G matrix, however, has the following structure

$${}^2G = \begin{pmatrix} {}^2G_{\alpha,\alpha}^{\alpha,\alpha} & {}^2G_{\beta,\beta}^{\alpha,\alpha} & 0 & 0 \\ {}^2G_{\alpha,\alpha}^{\beta,\beta} & {}^2G_{\beta,\beta}^{\beta,\beta} & 0 & 0 \\ 0 & 0 & {}^2G_{\alpha,\beta}^{\alpha,\beta} & 0 \\ 0 & 0 & 0 & {}^2G_{\beta,\alpha}^{\beta,\alpha} \end{pmatrix}. \quad (26)$$

Thus, the 2G matrix has three blocks with dimensions $2r_s^2$, r_s^2 , and r_s^2 respectively. For a closed-shell atom or molecule the $\alpha\alpha$ - and the $\beta\beta$ -blocks are the same, and the $\alpha\beta$ - and the $\beta\alpha$ -blocks are equal. However, because of the coupling between the $\alpha\alpha$ - and the $\beta\beta$ -blocks, this entire block must be kept positive semidefinite to enforce the complete 2G condition.

While the operators \hat{C} that form the basis functions of the 2D , 2Q , and 2G matrices are spin adapted for the \hat{S}_z operator, they are not spin adapted for the \hat{S}^2 operator. We can *spin adapt* these operators by forming linear combinations [45–47]. When the expectation value M of the z -component \hat{S}_z of the total spin angular momentum operator equals zero, each of the three 2-RDMs forms, the 2D , the 2Q , and the 2G matrices, divides into *four distinct spin-adapted blocks*. Using the total and z -component spin quantum numbers s and m of the operators \hat{C} , we can label these blocks as $|s, m\rangle = |0, 0\rangle$, $|1, -1\rangle$, $|1, 0\rangle$, and $|1, 1\rangle$.

In the 2D matrix the operators for the basis functions of the $\alpha\alpha$ and $\beta\beta$ blocks in Eq. (25),

$$|{}^D\Phi_{i,j}^{1,-1}\rangle = \hat{a}_{i,\alpha}\hat{a}_{j,\alpha}|\Psi\rangle \quad (27)$$

$$|{}^D\Phi_{i,j}^{1,1}\rangle = \hat{a}_{i,\beta}\hat{a}_{j,\beta}|\Psi\rangle, \quad (28)$$

are already spin-adapted. They represent $|s, m\rangle = |1, -1\rangle$ and $|1, 1\rangle$ respectively. In contrast, the operators for the basis functions of the $\alpha\beta$ block are a mixture of $|s, m\rangle = |0, 0\rangle$ and $|1, 0\rangle$. These basis functions may be resolved into these two spin-adapted sets of operators through the following linear combinations

$$|{}^D\Phi_{i,j}^{0,0}\rangle = \frac{1}{\sqrt{2}} (\hat{a}_{i,\alpha}\hat{a}_{j,\beta} + \hat{a}_{j,\alpha}\hat{a}_{i,\beta}) |\Psi\rangle \quad (29)$$

$$|{}^D\Phi_{i,j}^{1,0}\rangle = \frac{1}{\sqrt{2}} (\hat{a}_{i,\alpha}\hat{a}_{j,\beta} - \hat{a}_{j,\alpha}\hat{a}_{i,\beta}) |\Psi\rangle. \quad (30)$$

It is not difficult to show that the overlaps of the basis functions $|{}^D\Phi_{i,j}^{0,0}\rangle$ with basis functions $|{}^D\Phi_{i,j}^{1,0}\rangle$ vanish when $M = 0$.

The 2Q matrix has the same spin structure as the 2D matrix by particle-hole symmetry, but the 2G matrix has a different spin adaptation. The operators for the basis functions of the $\alpha\beta$ and $\beta\alpha$ blocks of the 2G matrix in Eq. (26),

$$|{}^G\Phi_{i,j}^{1,1}\rangle = \hat{a}_{i,\alpha}^\dagger \hat{a}_{j,\beta} |\Psi\rangle \quad (31)$$

$$|{}^G\Phi_{i,j}^{1,-1}\rangle = \hat{a}_{i,\beta}^\dagger \hat{a}_{j,\alpha} |\Psi\rangle, \quad (32)$$

are already spin-adapted with $|s, m\rangle = |1, 1\rangle$ and $|1, -1\rangle$ respectively. The basis functions of the remaining block of the 2G matrix, which mix operators from $|s, m\rangle = |0, 0\rangle$ and $|1, 0\rangle$, may be resolved into two spin-adapted sets as follows

$$|{}^G\Phi_{i,j}^{0,0}\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{i,\alpha}^\dagger \hat{a}_{j,\alpha} + \hat{a}_{i,\beta}^\dagger \hat{a}_{j,\beta} \right) |\Psi\rangle \quad (33)$$

$$|{}^G\Phi_{i,j}^{1,0}\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{i,\alpha}^\dagger \hat{a}_{j,\alpha} - \hat{a}_{i,\beta}^\dagger \hat{a}_{j,\beta} \right) |\Psi\rangle. \quad (34)$$

As in the case of the 2D matrix, when $M = 0$, the overlaps between basis functions $|{}^G\Phi_{i,j}^{0,0}\rangle$ and basis functions $|{}^G\Phi_{i,j}^{1,0}\rangle$ vanish. This reduces the largest block of the 2G matrix from $2r_s^2$ to r_s^2 .

An analogous spin adaptation may be performed for the partial 3-positivity matrices T_1 and T_2 . Spin adapting T_1 and T_2 is equivalent to spin adapting 3D and 3E from Eq. (13) respectively. For notational convenience we will present the spin adaptation of the 3D and 3E matrices. For the three-particle metric matrices 3D or 3E there are *at most six spin-adapted blocks* which may be denoted by $|s, m\rangle = |1/2, 1/2\rangle, |1/2, -1/2\rangle, |3/2, -3/2\rangle, |3/2, -1/2\rangle, |3/2, 1/2\rangle$ and $|3/2, 3/2\rangle$ where s and m are the spin quantum numbers of the \hat{C} operators that generate the basis functions. Spin adaptation has been considered for the 2D matrix [48–53] but not for the other metric matrices.

In the 3D matrix the operators for the basis functions of the $\alpha\alpha\alpha$ and $\beta\beta\beta$ blocks,

$$|{}^D\Phi_{i,j,k}^{3/2,-3/2}\rangle = \hat{a}_{i,\alpha} \hat{a}_{j,\alpha} \hat{a}_{k,\alpha} |\Psi\rangle \quad (35)$$

$$|{}^D\Phi_{i,j,k}^{3/2,3/2}\rangle = \hat{a}_{i,\beta} \hat{a}_{j,\beta} \hat{a}_{k,\beta} |\Psi\rangle, \quad (36)$$

are already spin-adapted, and they represent $|s, m\rangle = |3/2, -3/2\rangle$ and $|3/2, 3/2\rangle$ respectively. In contrast, the operators for the basis functions of the $\alpha\alpha\beta$ block, which are a mixture of

$|s, m\rangle = |3/2, -1/2\rangle$ and $|1/2, -1/2\rangle$, may be resolved into two spin-adapted sets as follows

$$|{}^D\Phi_{i,j,k}^{1/2,-1/2}\rangle = \frac{1}{\sqrt{2}}\hat{a}_{i,\alpha}(\hat{a}_{j,\alpha}\hat{a}_{k,\beta} + \hat{a}_{k,\alpha}\hat{a}_{j,\beta})|\Psi\rangle \quad (37)$$

$$|{}^D\Phi_{i,j,k}^{3/2,-1/2}\rangle = \frac{1}{\sqrt{2}}\hat{a}_{i,\alpha}(\hat{a}_{j,\alpha}\hat{a}_{k,\beta} - \hat{a}_{k,\alpha}\hat{a}_{j,\beta})|\Psi\rangle, \quad (38)$$

and similarly, the operators for the basis functions of the $\alpha\beta\beta$ block may be resolved into two spin-adapted sets

$$|{}^D\Phi_{i,j,k}^{1/2,1/2}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{i,\alpha}\hat{a}_{j,\beta} + \hat{a}_{j,\alpha}\hat{a}_{i,\beta})\hat{a}_{k,\beta}|\Psi\rangle \quad (39)$$

$$|{}^D\Phi_{i,j,k}^{3/2,1/2}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{i,\alpha}\hat{a}_{j,\beta} - \hat{a}_{j,\alpha}\hat{a}_{i,\beta})\hat{a}_{k,\beta}|\Psi\rangle. \quad (40)$$

An equivalent spin adaptation exists for the hole matrix 3Q .

In the 3E matrix the operators for the basis functions of the $\beta\alpha\alpha$ and $\alpha\beta\beta$ blocks,

$$|{}^E\Phi_{i,j,k}^{3/2,-3/2}\rangle = \hat{a}_{j,\beta}^\dagger\hat{a}_{i,\alpha}\hat{a}_{k,\alpha}|\Psi\rangle \quad (41)$$

$$|{}^E\Phi_{i,j,k}^{3/2,3/2}\rangle = \hat{a}_{j,\alpha}^\dagger\hat{a}_{i,\beta}\hat{a}_{k,\beta}|\Psi\rangle, \quad (42)$$

are already spin-adapted, and they correspond to $|s, m\rangle = |3/2, -3/2\rangle$ and $|3/2, 3/2\rangle$. The basis functions whose operators are a mixture of $|s, m\rangle = |3/2, 1/2\rangle$ and $|1/2, 1/2\rangle$ may be resolved into two spin-adapted sets as follows

$$|{}^E\Phi_{i,j,k}^{1/2,-1/2}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{j,\alpha}^\dagger\hat{a}_{k,\alpha} + \hat{a}_{j,\beta}^\dagger\hat{a}_{k,\beta})\hat{a}_{i,\alpha}|\Psi\rangle \quad (43)$$

$$|{}^E\Phi_{i,j,k}^{3/2,-1/2}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{j,\alpha}^\dagger\hat{a}_{k,\alpha} - \hat{a}_{j,\beta}^\dagger\hat{a}_{k,\beta})\hat{a}_{i,\alpha}|\Psi\rangle. \quad (44)$$

Basis functions whose operators are a mixture of $|s, m\rangle = |3/2, -1/2\rangle$ and $|1/2, -1/2\rangle$ may be separated by analogous linear combinations. A similar spin adaptation exists for the matrix 3F .

For any singlet wavefunction ($S = 0$ and $M = 0$) the three basis functions labeled by $m = -1, 0, 1$ and $s = 1$ in each of the three 2-positive metric matrices are equivalent. Hence, only two distinct spin blocks for each of the 2D , 2Q , and 2G matrices need to be constrained to be positive semidefinite. Unlike the case for the 2-RDMs, it may be an assumption for the 3-RDMs that basis functions with the same m but different s are orthogonal. With this assumption in the singlet case, however, the 3-positive basis functions with the same s yield equivalent metric matrices, and there are only two distinct spin blocks, corresponding to $s = 1/2$ and $s = 1/2$, for the 3-positive metric matrices as well as for the T_1 and T_2 matrices.

While all molecules have spin symmetry, many molecules also possess spatial symmetry. If a molecule has *point-group symmetry*, then each spin block of each RDM metric matrix may be further decomposed into smaller blocks whose basis functions are contained in different irreducible representations of the point group. We refer to this further decomposition of the RDMs as *symmetry adaptation*. Restraining a larger number of smaller blocks to be semidefinite computationally facilitates the solution of the semidefinite program for both first- and second-order algorithms.

III. APPLICATIONS

After a summary of the implemented N -representability conditions and the optimization algorithm, we apply the variational 2-RDM method to compute the ground-state energies for several molecules as well as the ground-state potential energy curves for the molecules BH, HF, and N₂.

A. Summary of N -representability constraints

Here we summarize the N -representability conditions which we employ for computing the 2-RDM for a singlet ground-state wavefunction:

(1) The Hermiticity condition:

$${}^2D_{k,l}^{i,j} = {}^2D_{i,j}^{k,l}. \quad (45)$$

(2) The antisymmetry of the 2-RDM indices

$${}^2D_{k,l}^{i,j} = -{}^2D_{k,l}^{j,i}, \quad (46)$$

is enforced by a unitary transformation to antisymmetrized basis functions

$$\tilde{\phi}_{i,j}(1,2) = \frac{1}{\sqrt{2}} (\phi_{i,j}(1,2) - \phi_{j,i}(1,2)).$$

(3) The trace conditions [49]:

$$\begin{aligned} N_s(N_s + 1) &= \text{Tr}({}^2D_{S=0}) \\ N_s(N_s - 1) &= \text{Tr}({}^2D_{S=1}) \end{aligned} \quad (47)$$

where $N_s = N/2$.

(4) 2-positivity and T_2 conditions for the 2-RDM:

$$\{^2D \geq 0, ^2Q \geq 0, ^2G \geq 0, T_2 \geq 0\}. \quad (48)$$

(5) Mappings expressing the Q- and the G-matrices in terms of the D matrix.

(6) Contraction conditions between the 2-RDM and the 1-RDM:

$$\begin{aligned} (N_s + 1)^1D_{k,\alpha}^{i,\alpha} &= \sum_j ^2D_{S=0}^{i,j;k,j} \\ (N_s - 1)^1D_{k,\alpha}^{i,\alpha} &= \sum_j ^2D_{S=1}^{i,j;k,j}. \end{aligned} \quad (49)$$

Constraints (1-3) define a generic fermionic density matrix but not necessarily a reduced density matrix, and constraints (4-6) enforce the 2-positivity conditions and the T_2 partial 3-positivity condition.

B. Optimization algorithm

To solve the variational 2-RDM minimization, we convert the semidefinite program into a constrained nonlinear optimization [29, 30]. The metric matrices M are factorized as follows

$$M = RR^* \quad (50)$$

to constrain them to be positive semidefinite. With these factorizations the linear mappings, relating the 2D , 2Q , 2G , and T_2 metric matrices, become quadratic (or nonlinear) equalities. Rosina [54], Harriman [6], and Mazziotti [12] previously considered matrix factorizations for reduced density matrices, and Burer and Monteiro [55] recently employed matrix factorizations for solving large-scale problems in combinatorial optimization. We solve the resulting constrained nonlinear optimization problem by an augmented Lagrangian multiplier method [29, 30, 55, 56]. The resulting first-order algorithm for semidefinite programming (SDP) is called RRSQP in reference to the matrix factorization in Eq. (50). Within RRSQP the initial elements of the 2-RDM metric matrices are selected with a random number generator; hence, neither the final nor the initial 2-RDM depends upon the choice of a reference wavefunction. Variational 2-RDM calculations are performed with RRSQP except for BH where we also present the energies from SeDuMi, a package which implements a second-order primal-dual interior-point algorithm [57]. The first-order algorithm is significantly

more efficient than the interior-point algorithms in both memory requirements and floating-point operations. Further details of the first-order, nonlinear algorithm for calculating the 2-RDM as well as comparisons with the primal-dual interior-point algorithms may be found in references [29, 30].

C. Calculations

For each molecule in Table I the error in the ground-state energy in a minimal Slater-type orbital (STO-6G) basis set is reported for the variational 2-RDM method with two sets of constraints, the 2-positivity conditions (DQG) and the 2-positivity as well as T_2 conditions (DQGT2). These energies are compared to several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with perturbative triples (CCSD(T)) and full configuration interaction (FCI). Throughout this section equilibrium geometries for molecules are taken from the *Handbook of Chemistry and Physics* [59], and one- and two-electron integrals as well as the energies from wavefunction methods are computed with the quantum chemistry packages GAMESS (USA) [60] and Gaussian [61]. The energies for the RDM methods are lower than the FCI results, as expected for incomplete constraints, but the “overshoot” is less when the T_2 condition is added. In general the ground-state 2-RDM energies with the DQGT2 conditions are an order of magnitude better than the energies with only the DQG conditions. These calculations corroborate the results of Zhao et al [37]. The DQGT2 energies are similar in accuracy to the coupled cluster methods. The largest errors in the 2-RDM energies occur for molecules like NH_3 and CH_4 with sp^3 hybridization and N_2 with a triple bond.

Table II and Figure 1 examine the potential energy curve of the BH molecule in an STO-6G basis set with a frozen core. Previous calculations with the 2-RDM method with DQGT2 conditions have been restricted to studying molecules at equilibrium geometries [37]. Figure 1 shows that the 2-RDM method with the DQGT2 constraints yields a curve which is indistinguishable from the FCI curve for BH at all bond lengths. In Table II the errors in the energies are reported at selected bond lengths. Two sets of errors, labeled SeDuMi [57] and RRSDP [29, 30] to denote the algorithm employed for solving the semidefinite program, are reported for both the DQG and the DQGT2 constraints. The RRSDP algorithm offers

TABLE I: For atoms and molecules in minimal STO-6G basis sets the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI).

System	FCI Energy	Error in the Ground-state Energy (mH)					
		Wave Function Methods				2-RDM Methods	
		HF	MP2	CCSD	CCSD(T)	DQG	DQGT2
BH	-25.059317	57.8	28.3	0.2	0.1	-3.7	-0.1
BeH ₂	-15.759020	35.8	12.1	0.4	0.2	-1.1	-0.2
CH ₂	-38.805247	59.0	24.6	0.5	0.3	-12.2	-0.0
H ₂ O	-75.728766	50.0	14.1	0.0	-0.0	-1.7	-0.1
NH ₃	-56.054413	66.1	18.2	0.2	0.1	-9.8	-0.7
CH ₄	-40.190589	80.2	23.0	0.2	0.1	-19.3	-1.4
N ₂	-108.700534	158.7	2.8	4.0	2.2	-12.2	-1.9

significant savings in memory usage and floating-point operations although the primal-dual interior-point algorithm, when applicable despite its computational cost, can usually be converged to a greater number of significant digits. As Table II shows, both algorithms give essentially identical errors for the DQG conditions, but they differ for the DQGT2 conditions where SeDuMi converges to the FCI values within 20 μ H. For BH in this basis set realizing the accuracy of the DQGT2 positivity conditions requires convergence of the ground-state energy to about 6 or 7 decimals. The maximum error on the potential energy curve from the 2-RDM method with the DQGT2 conditions is more than an order of magnitude smaller than for either CCSD or CCSD(T).

Breaking the triple bond of nitrogen is a challenging correlation problem that requires at least six-particle excitations from the Hartree-Fock reference. Table III and Figure 2 examine the potential energy curve of the N₂ molecule in an STO-6G basis set with a frozen core. Both 2-RDM methods have their maximum errors around 1.7 Å and become very accurate in the dissociation limit. The maximum error of -23.6 mH for 2-positivity is improved

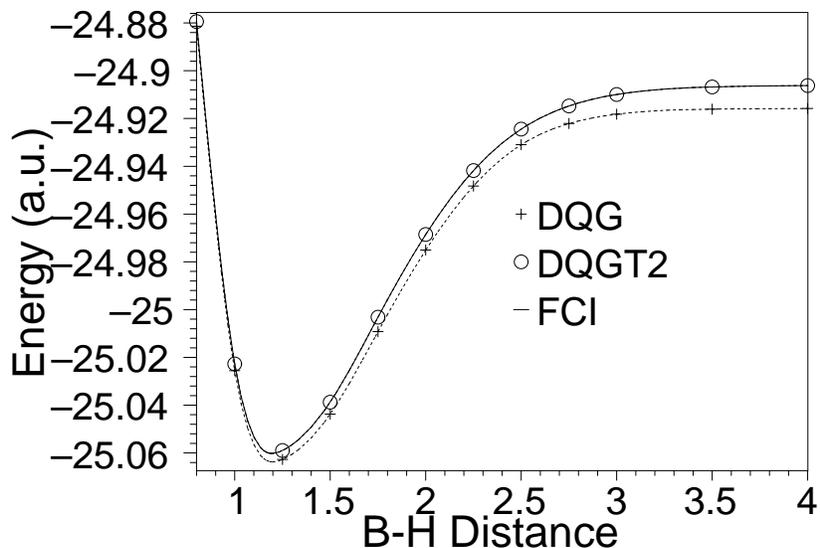


FIG. 1: The 2-RDM method with the DQGT2 constraints yields a curve which is indistinguishable from the FCI curve for BH at all bond lengths.

to -5.0 mH for DQGT2. Both second-order perturbation theory and the coupled cluster methods diverge between 1.7 and 2 Å. Figure 2 compares the 2-RDM methods with DQG and DQGT2 as well as CCSD in the bonding region and at intermediate stretches. Around equilibrium the DQGT2 method improves upon the energy errors of DQG and CCSD by factors of five and two respectively.

For each molecule in Table IV the error in the ground-state correlation energy in a valence double-zeta basis set [58] is reported for the variational 2-RDM method applied with two sets of constraints, the 2-positivity conditions (DQG) and the 2-positivity as well as T2 conditions (DQGT2). The DQGT2 conditions have not previously been applied to non-minimal basis sets. Equilibrium geometries for molecules are taken from the *Handbook of Chemistry and Physics* [59]. As in the minimal basis set results, the ground-state 2-RDM energies with the DQGT2 conditions are generally an order of magnitude better than the energies with the DQG conditions alone and similar in accuracy to the coupled cluster methods. For the DQGT2 method the largest error in the 2-RDM energies -4.1 mH occurs for N₂ with its triple bond.

For selected bond distances along the potential energy curve of HF in a valence double-zeta basis set [58] the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T₂ conditions (DQGT2) are compared

TABLE II: For selected bond distances along the potential energy curve of BH in a minimal STO-6G basis set the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI). For the 2-RDM methods energies are reported for solving the semidefinite program both by a primal-dual interior-point algorithm (SeDuMi) and by the first-order, nonlinear method (RRSDP) in reference [29]. The 2-RDM method with DQGT2 conditions yields energies throughout the potential curve which are accurate within $20 \mu\text{H}$.

		Error in the Ground-state Energy (mH)							
		Wave Function Methods				2-RDM Methods			
Bond	FCI					RRSDP	SeDuMi	RRSDP	SeDuMi
Length	Energy	HF	MP2	CCSD	CCSD(T)	DQG		DQGT2	
0.80	-24.879413	49.82	26.48	0.33	0.16	-2.00	-1.99	-0.11	-0.00
1.25	-25.058962	58.12	28.68	0.15	0.11	-3.76	-3.77	-0.04	-0.00
1.50	-25.038739	69.40	33.51	0.16	0.11	-5.00	-5.00	-0.11	-0.01
1.75	-25.003159	85.82	41.17	0.17	0.11	-6.06	-6.07	-0.08	-0.01
2.00	-24.968552	107.51	51.63	0.15	0.07	-6.53	-6.52	-0.05	-0.02
2.50	-24.924413	162.95	76.40	0.07	0.00	-6.56	-6.56	-0.03	-0.02
3.00	-24.909945	217.30	88.67	-0.01	0.08	-8.25	-8.25	-0.02	-0.01
4.00	-24.906234	278.00	45.23	-0.01	0.34	-9.60	-9.60	-0.01	-0.00

in Table V with the energies from several wavefunction methods. The core orbital of fluorine is frozen. In the region around its equilibrium geometry the energies from the 2-RDM method with DQGT2 conditions are as accurate as the energies from coupled cluster with a perturbative triples correction (CCSD(T)). Although the absolute magnitude of the error in the energy increases with bond distance for all approximate methods considered, it remains the smallest in the 2-RDM method with DQGT2 constraints as shown in Figure 3.

Table VI and Figure 4 examine the potential energy curve of the N_2 molecule in valence

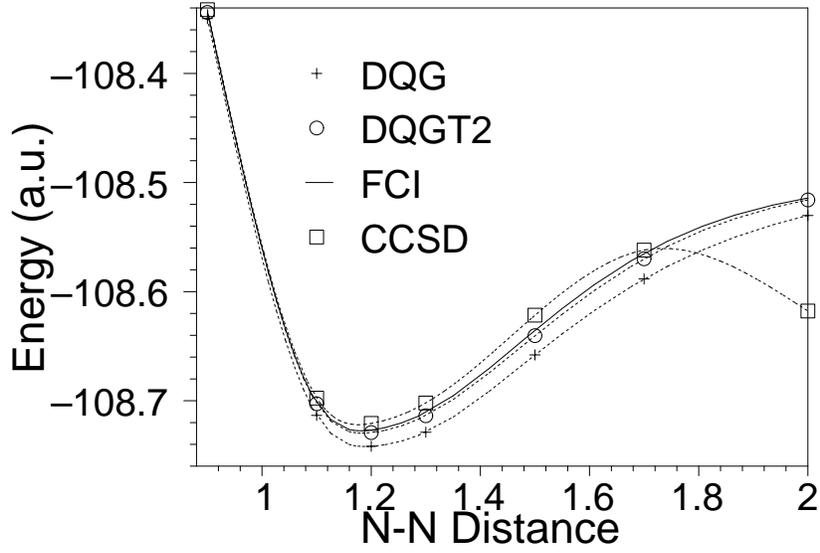


FIG. 2: The 2-RDM methods with DQG and DQGT2 as well as CCSD are compared in the bonding region and at intermediate stretches. Around equilibrium the DQGT2 method improves upon the energy errors of DQG and CCSD by factors of five and two respectively.

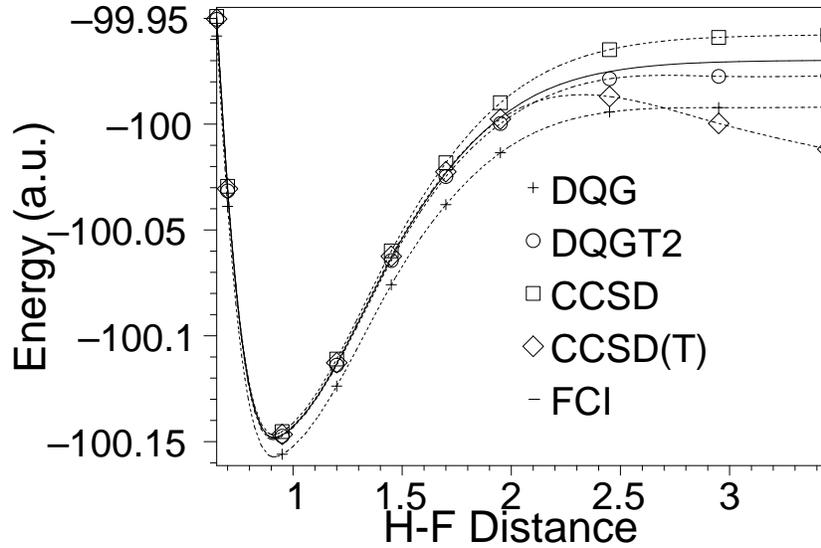


FIG. 3: Potential energy curves of HF are generated in a valence double-zeta basis set from the two variational 2-RDM methods, one with the 2-positivity conditions (DQG) and one with both the 2-positivity and the T_2 conditions (DQGT2). Although the absolute magnitude of the error in the energy increases with bond distance for all approximate methods considered, it remains the smallest in the 2-RDM method with DQGT2 constraints.

TABLE III: For selected bond distances along the potential energy curve of N_2 in a minimal STO-6G basis set the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI). While perturbation theory and both coupled cluster methods diverge between 1.7 and 2 Å, both variational 2-RDM methods correctly predict the energy of the dissociated molecule. The 2-RDM method with DQGT2 conditions has its maximum error of -5 mH around 1.7 Å.

Bond Length		Error in the Ground-state Energy (mH)					
		Wave Function Methods				2-RDM Methods	
		FCI	HF	MP2	CCSD	CCSD(T)	DQG
0.9	-108.343278	107.1	9.3	1.8	0.7	-6.5	-0.8
1.2	-108.726855	191.2	-5.9	6.0	3.9	-14.9	-2.3
1.5	-108.635450	311.3	-67.7	13.8	10.9	-22.5	-4.9
1.7	-108.564861	412.0	-143.5	3.0	-0.0	-23.6	-5.0
2.0	-108.514262	585.6	-318.1	-103.5	-110.2	-15.9	-1.6
2.5	-108.499969	825.8	-840.5	nc ^a	nc ^a	-3.1	-0.1
3.0	-108.498495	959.5	-1587.9	nc ^a	nc ^a	-0.3	-0.0
4.0	-108.498241	1065.8	-3220.8	nc ^a	nc ^a	-0.0	-0.0

^aThe abbreviation nc indicates that the calculation did not converge.

double-zeta [58] with one frozen core and virtual orbital for each nitrogen atom. Both 2-RDM methods have their maximum errors around 1.75 Å with a realistic description of the dissociation. The maximum error of -60.6 mH for 2-positivity is improved to -13.9 mH for DQGT2. Single-reference many-body perturbation theory and coupled cluster methods diverge before 2 Å. The positivity conditions provide a “multi-referenced” approximation to the N -representable set of 2-RDMs. Figure 4 compares the 2-RDM methods with DQG and DQGT2 as well as CCSD and CCSD(T) for stretched geometries between 1.6 Å and 3.3 Å.

TABLE IV: For atoms and molecules in valence double-zeta basis sets the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI). All valence electrons are correlated; two, three, and four virtual orbitals are frozen on N_2 , NH_3 , and CH_4 . The addition of the T2 condition to the 2-RDM method improves the energies by an order of magnitude.

System	FCI Energy	Error in the Ground-state Energy (mH)					
		Wave Function Methods				2-RDM Methods	
		HF	MP2	CCSD	CCSD(T)	DQG	DQGT2
BH	-25.173472	60.1	23.9	0.8	0.3	-4.5	-0.0
BeH ₂	-15.800200	40.0	11.8	0.4	0.2	-1.4	-0.2
CH ₂	-38.946456	85.1	23.3	1.9	0.6	-16.4	-0.1
H ₂ O	-76.141126	132.0	8.0	1.7	0.5	-14.9	-1.8
NH ₃	-56.249856	74.1	8.0	1.1	0.2	-10.6	-1.6
CH ₄	-40.244195	58.7	8.3	0.6	0.1	-8.8	-1.2
N ₂	-109.038938	160.9	16.3	6.3	1.8	-31.1	-4.1

IV. DISCUSSION AND CONCLUSIONS

The variational 2-RDM method with 2-positivity conditions, applied to a variety of atoms and molecules, yields energies with consistent accuracy at both equilibrium and non-equilibrium geometries [20–22, 24, 29–32]. Additional accuracy may be achieved by including higher positivity conditions within the optimization. Two distinct sets of partial 3-positivity conditions have been proposed: (i) the lifting conditions [20, 36] and (ii) the T_1 and T_2 conditions [5, 37]. Within the present paper we have implemented a spin- and symmetry-adapted T_2 condition in a first-order, nonlinear semidefinite programming algorithm [29, 30] for optimizing the energy with the 2-RDM. With this implementation we are able to treat molecules in non-minimal basis sets and at stretched geometries.

Supplementing the 2-positivity conditions with the T_2 constraint in a variational 2-RDM

TABLE V: For selected bond distances along the potential energy curve of HF in a valence double-zeta basis set the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI). In the region around its equilibrium geometry the energies from the 2-RDM method with DQGT2 conditions are as accurate as the energies from coupled cluster with a perturbative triples correction (CCSD(T)). The energies from the CCSD(T) technique diverge around 2 Å. Although the absolute magnitude of the error in the energy increases with bond distance for all approximate methods considered, it remains the smallest in the 2-RDM method with DQGT2 constraints.

Bond		Error in the Ground-state Energy (mH)					
		Wave Function Methods				2-RDM Methods	
Length	FCI	HF	MP2	CCSD	CCSD(T)	DQG	DQGT2
0.70	-100.030677	109.7	4.1	1.3	0.2	-8.1	-0.8
0.95	-100.146927	126.0	3.7	1.7	0.3	-9.1	-0.5
1.20	-100.113294	141.6	4.9	2.3	0.6	-10.5	-0.5
1.45	-100.063240	158.7	8.7	3.3	0.8	-12.6	-1.2
1.95	-99.996779	203.7	25.1	6.9	-0.8	-16.7	-2.9
2.45	-99.975146	256.5	42.9	10.4	-11.8	-19.1	-3.4
2.95	-99.970696	348.4	41.8	11.7	-29.0	-21.5	-6.7
3.45	-99.969888	402.5	20.1	12.0	-41.9	-22.1	-7.3

calculation improves the accuracy of the resulting ground-state energy by one or more orders of magnitude. The 2-RDM technique with 2-positivity conditions yields consistent accuracy at equilibrium geometries as well as non-equilibrium geometries where multiple reference determinants strongly contribute [20–22, 24, 29–32]. This significant attribute persists in the 2-RDM calculations with the T_2 condition. Accurate potential energy curves are computed with the T_2 restriction for BH, HF, and N_2 . The positivity conditions define a convex set of two-electron density matrices that well approximates the convex set of N -representable two-

TABLE VI: For selected bond distances along the potential energy curve of N_2 in a valence double-zeta basis set the ground-state energies from the variational 2-RDM method with 2-positivity conditions (DQG) as well as 2-positivity and T_2 conditions (DQGT2) are compared with the energies from several wavefunction methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), coupled-cluster singles-doubles with a perturbative triples correction (CCSD(T)) and full configuration interaction (FCI). While perturbation theory and coupled cluster methods diverge between 1.75 and 2 Å, the variational 2-RDM methods display similar accuracy at equilibrium and highly stretched geometries. The 2-RDM method with the DQGT2 conditions has its maximum error of -13.9 mH around 1.5 Å. The bond length R_c equals 1.094363636 Å.

Bond		Error in the Ground-state Energy (mH)					
		Wave Function Methods				2-RDM Methods	
Length	FCI	HF	MP2	CCSD	CCSD(T)	DQG	DQGT2
0.75 R_c	-108.500949	114.6	13.7	2.5	0.6	-23.3	-2.6
1.00 R_c	-109.038938	160.9	16.3	6.3	1.8	-31.1	-4.1
1.25 R_c	-108.984133	236.1	-0.6	14.1	4.2	-45.3	-10.6
1.50 R_c	-108.902296	351.6	-69.6	27.3	4.9	-58.2	-13.9
1.75 R_c	-108.848476	465.8	-16.1	10.1	-47.3	-60.6	-13.8
2.00 R_c	-108.828810	577.6	-284.2	-79.2	-226.1	-53.3	-13.1
2.50 R_c	-108.820667	746.2	-663.9	-150.6	-415.4	-39.2	-8.1
3.00 R_c	-108.817763	845.4	-1185.5	-163.7	-468.1	-33.8	-6.1

electron density matrices. Because the 2-RDM for each N -electron wavefunctions regardless of its correlation is contained in the approximate set, the variational 2-RDM method can capture multi-reference behavior that is difficult to describe in an approximate parametrization of the many-electron wavefunction. The 2-RDM method does not use a reference wavefunction to describe the electron correlation or to provide an initial guess for the 2-RDM. The initial elements of the 2-RDM metric matrices are selected randomly.

The number of floating-point operations in the variational 2-RDM method with 2-positivity conditions scales approximately in floating-point operations and memory as r_s^{16}

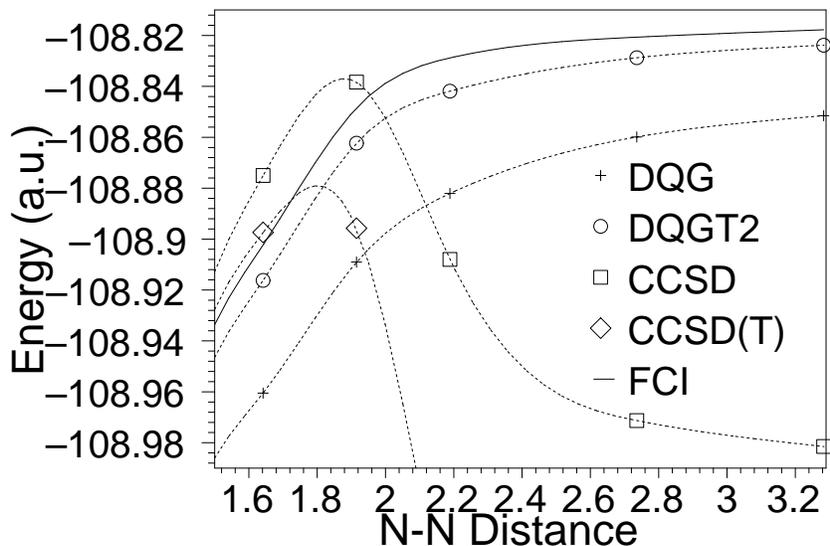


FIG. 4: The 2-RDM methods with DQG and DQGT2 as well as CCSD and CCSD(T) are compared for N_2 at stretched geometries in a valence double-zeta basis set.

and r_s^8 respectively in the primal-dual interior-point algorithm for semidefinite programming but as r_s^6 and r_s^4 in the first-order, nonlinear algorithm where r_s is the number of spatial orbitals [29, 30]. Addition of the T_2 condition in the interior-point method produces a scaling of r_s^{24} and r_s^{12} in floating-point operations and memory. Zhao et al. [37] reformulate the semidefinite program for interior-point codes to achieve a floating-point scaling of r_s^{12} and a storage cost of r_s^8 . A similar addition of the T_2 constraint in the first-order algorithm yields a scaling of r_s^9 and r_s^6 . The spin and symmetry adaptation of the 2-RDM metric matrices, which we derive and implement, further reduces the cost of the algorithm, especially for molecules with spatial symmetry. While the computational scaling of the first-order algorithm is better than that of the second-order, interior-point methods, the scaling in floating-point operations presently limits the applicability of the T_2 condition to larger molecules and basis sets. Future work will explore further improving the scaling and efficiency of the T_2 condition as well as using other partial 3-positivity conditions such as the lifting conditions [20, 36].

The present calculations demonstrate that the variational 2-RDM method with the 2-positivity and T_2 conditions yields accurate energies in non-minimal basis sets at both equilibrium and stretched geometries. The 2-RDM method, while still in development, offers a new lower-bound approach to treating correlated quantum systems in chemistry and physics

without constructing or parameterizing a many-electron wavefunction.

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