Variational two-electron reduced-density-matrix theory: Partial 3-positivity conditions for *N*-representability

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Variationally calculating the ground state of a many-electron quantum system using only the two-electron reduced-density-matrix (2-RDM) requires *N*-representability conditions that constrain the 2-RDM to correspond to an *N*-electron wave function. A systematic hierarchy of *N*-representability conditions, known as *p*-positivity conditions, has been developed [D. A. Mazziotti and R. M. Erdahl, Phys. Rev. A **63**, 042113 (2001)], and many-electron atoms and molecules in nonminimal basis sets have been solved with useful accuracy by a variational 2-RDM method with 2-positivity conditions [D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004)]. This paper considers two forms of *partial* 3-positivity conditions, the lifting conditions and the T_1/T_2 conditions, to further enhance the accuracy of the 2-RDM methods without the computational cost of full 3-positivity conditions. Variational 2-RDM methods with different *N*-representability constraints including 2-positivity conditions, the two types of partial 3-positivity conditions, as well as the complete 3-positivity conditions are applied to compute the ground state of the Lipkin spin model. The energies and 2-RDMs are compared to the results from full and truncated configuration interaction, many-body perturbation theory, and couple cluster theory with single and double excitations. Implications of using partial 3-positivity for variational 2-RDM calculations of many-electron atoms and molecules will be discussed.

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I. INTRODUCTION

Although a two-particle reduced density matrix (2-RDM) provides most of the useful information contained in the *N*-electron wave function [1], direct minimization of the energy as a functional of the 2-RDM has been elusive because the 2-RDM must be constrained to correspond to an *N*-electron system where the search for the appropriate conditions has been called the *N*-representability problem [2–4]. Significant progress in the realization of the variational 2-RDM method has been made along two fronts with the development of: (i) a systematic hierarchy for enforcing the approximate *N*-representability of the 2-RDM [5–9] and (ii) new optimization algorithms for minimizing the energy with respect to a 2-RDM constrained by positivity conditions [5,10–21].

Three different representations of the 2-RDM for a many-electron system should be constrained to be *positive semidefinite* where a matrix is positive semidefinite if and only if all of its eigenvalues are non-negative. These necessary restrictions, known as the 2-*positivity conditions*, were originally derived by Garrod and Percus [5]. A variational 2-RDM method with the 2-RDM restricted by 2-positivity conditions was applied to Be and He_2 in the 1970s. The minimization of the energy subject to several matrices constrained to be positive semidefinite constitutes an optimization problem known as a semidefinite program. Using interior-point methods developed in the 1990s, Nakatsuji and co-workers [11,14] and Mazziotti [12,13] applied a variational 2-RDM method to compute the ground-state energies of atoms and molecules in equilibrium and nonequilibrium geometries. Calculations of bond stretching and dissociation showed that the 2-RDM method treats both single- and multi-reference correlation effects with similar accuracy [12–14,16,19,20]. Multireference effects, which arise when multiple reference determinants contribute significantly to the correlated wave function, are difficult to treat with traditional approaches to electron correlation and yet are especially important for describing nonequilibrium geometries as in transition-state structures and dissociation.

Erdahl and Jin [7] and Mazziotti and Erdahl [8] generalized the 2-positivity conditions to *p*-positivity conditions in which $p+1$ *p*-particle matrices are constrained to be positive semidefinite. The *p*-positivity conditions enforce the generalized uncertainty relations for all $p/2$-body operators [8]. Using a spin model, Mazziotti and Erdahl demonstrated that 3-positivity produced highly accurate correlation energies for correlation strengths where perturbative methods fail. A partial set of 3-positivity conditions was derived by Mazziotti [12] using lifting operators; applications of only a portion of these partial 3-positivity restrictions, which we call *lifting conditions*, to BH improved upon the accuracy of 2-positivity. Recently, Zhao *et al.* [18] applied another subset of 3-positivity, proposed by Erdahl [6] and achieved an order of magnitude increase in accuracy for molecular ground-state energies.

The goals of the present paper are (i) to develop further the partial 3-positivity constraints known as the lifting conditions [12], (ii) to compare these partial 3-positivity conditions with the conditions proposed by Erdahl [6], and (iii) to examine both sets of partial 3-positivity conditions by application to the Lipkin quasispin model for which exact solutions are known. The lifting conditions arise from inserting projection operators for the 1-particle basis set into the metric matrices that generate the *D*, *Q*, and *G* conditions of 2-positivity. These conditions comprise an incomplete subset of the 3-positivity conditions and yet, computationally, they are much less expensive both in storage and floating-point

operations. The partial 3-particle positivity conditions perform well on the Lipkin model. Implications of using partial 3-positivity within a variational 2-RDM method for atomic and molecular calculations will be discussed.

II. THEORY

The energy for a system of N indistinguishable particles with p-particle interactions may be written as a linear functional of the p-RDM,

$$E = \mathrm{Tr}[H^N D] = \mathrm{Tr}[{}^pK^pD], \tag{1}$$

where ${}^pK$ is the p-particle reduced Hamiltonian matrix and the p-RDM is defined as

$${}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p} = \langle\Psi|\hat{a}^\dagger_{i_1}\hat{a}^\dagger_{i_2}\cdots\hat{a}^\dagger_{i_p}\hat{a}_{j_p}\cdots\hat{a}_{j_2}\hat{a}_{j_1}|\Psi\rangle \tag{2}$$

in second quantization. For each type of Hamiltonian there is a minimum value of p. In particular, for electronic systems p must be at least 2. Direct minimization of the energy in Eq. (1) with respect to the p-RDM requires N-representability conditions on the p-RDM to ensure that it derives from an N-particle density matrix. For atoms and molecules, because electrons interact pairwise, we are interested in the N-representability conditions for the 2-RDM.

A. Positivity conditions via metric matrices

Different representations of the p-RDMs are easily defined within second quantization. Consider the metric (or overlap) matrices M,

$$M^i_j = \langle\Phi_i|\Phi_j\rangle = \langle\Psi|\hat{C}_i\hat{C}^\dagger_j|\Psi\rangle, \tag{3}$$

from the set of basis functions

$$\langle\Phi_i| = \langle\Psi|\hat{C}_i, \tag{4}$$

where each $\hat{C}_i$ is a product of p creation and/or annihilation operators. When the $\hat{C}_i$ are products of p creation operators, the metric matrix in Eq. (4) becomes the definition for the p-RDM in Eq. (2). However, there are p additional metric matrices where the $\hat{C}_i$ are products of p second-quantized operators with different numbers of creation and annihilation operators. These $p+1$ metric matrices may be interconverted by rearranging the creation and annihilation operators, and each of the metric matrices must be positive semidefinite. We refer to restricting all $p+1$ metric matrices to be positive semidefinite as the p-positivity conditions [8]. The three metric matrices of 2-positivity can be generated from the operators $\hat{C}_i$ that are products of two creation operators, two annihilation operators, and one creation and one annihilation operator. Explicitly, the three metric matrices of 2-positivity, known as the D-, Q-, and G-matrices, are given by

$${}^2D^{ij}_{kl} = \langle\Phi^D_{ij}|\Phi^D_{kl}\rangle = \langle\psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_l\hat{a}_k|\psi\rangle, \tag{5}$$

$${}^2Q^{ij}_{kl} = \langle\Phi^Q_{ij}|\Phi^Q_{kl}\rangle = \langle\psi|\hat{a}_i\hat{a}_j\hat{a}^\dagger_l\hat{a}^\dagger_k|\psi\rangle, \tag{6}$$

$${}^2G^{ik}_{lj} = \langle\Phi^G_{ik}|\Phi^G_{lj}\rangle = \langle\psi|\hat{a}^\dagger_i\hat{a}_k\hat{a}^\dagger_j\hat{a}_l|\psi\rangle, \tag{7}$$

where $|\Phi^D_{kl}\rangle$, $|\Phi^Q_{kl}\rangle$, and $|\Phi^G_{kl}\rangle$, are $(N-2)$-, $(N+2)$-, and N-particle basis functions, respectively.

The four metric matrices of 3-positivity [8] can be written as

$${}^3D^{ijk}_{lmn} = \langle\psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}^\dagger_k\hat{a}_n\hat{a}_m\hat{a}_l|\psi\rangle, \tag{8}$$

$${}^3E^{ijk}_{lmn} = \langle\psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_k\hat{a}^\dagger_n\hat{a}_m\hat{a}_l|\psi\rangle, \tag{9}$$

$${}^3F^{ijk}_{lmn} = \langle\psi|\hat{a}^\dagger_i\hat{a}_j\hat{a}_k\hat{a}^\dagger_n\hat{a}^\dagger_m\hat{a}_l|\psi\rangle, \tag{10}$$

$${}^3Q^{ijk}_{lmn} = \langle\psi|\hat{a}_i\hat{a}_j\hat{a}_k\hat{a}^\dagger_n\hat{a}^\dagger_m\hat{a}^\dagger_l|\psi\rangle, \tag{11}$$

where ${}^3D$ and ${}^3Q$ are the 3-particle and 3-hole reduced density matrices, respectively, and ${}^3E$ and ${}^3F$ are 3-particle generalizations of the ${}^2G$ matrix.

B. The lifted conditions

The lifted 3-RDMs [12] are defined by taking the expectation values of particle (or hole) projection operators $\hat{n}_k = \hat{a}^\dagger_k\hat{a}_k$ (or $1-\hat{n}_k = \hat{a}_k\hat{a}^\dagger_k$) over the space spanned by the basis functions in Eqs. (5)–(7). An example of this type of expectation value is

$$\langle\Phi^D_{ij}|(1-\hat{n}_k)|\Phi^D_{lm}\rangle = \langle\Psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_k\hat{a}^\dagger_k\hat{a}_m\hat{a}_l|\Psi\rangle, \tag{12}$$

which is the ${}^3E$ matrix in Eq. (9) with $k=n$. Summing over the particle projection operators for all orbital basis functions gives the number operator $\hat{N}_k = \Sigma_k\hat{n}_k$. Hence because Eq. (12) contracts to the G-condition, it includes the N-representability restrictions from the G-condition as well as additional constraints [12]. The lifted conditions are part of the 3-positivity conditions since every principle submatrix of a positive semidefinite matrix must also be positive semidefinite [22]. By inserting either the particle or hole projection (or lifting) operator between the basis functions $|\Phi^D\rangle$, we generate two lifted metric matrices ${}^3D$ and ${}^3E$. Similarly, from the basis functions for ${}^2Q$ and ${}^2G$ we generate four more conditions for a total of *six* partial 3-positive conditions:

$$\langle\Phi^D_{ij}|\hat{a}^\dagger_k\hat{a}_k|\Phi^D_{lm}\rangle = \langle\Psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}^\dagger_k\hat{a}_k\hat{a}_m\hat{a}_l|\Psi\rangle = {}^3D^{ijk}_{lmk}, \tag{13}$$

$$\langle\Phi^D_{ij}|\hat{a}_k\hat{a}^\dagger_k|\Phi^D_{lm}\rangle = \langle\Psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_k\hat{a}^\dagger_k\hat{a}_m\hat{a}_l|\Psi\rangle = {}^3E^{ijk}_{lmk}, \tag{14}$$

$$\langle\Phi^G_{ij}|\hat{a}^\dagger_k\hat{a}_k|\Phi^G_{lm}\rangle = \langle\Psi|\hat{a}^\dagger_i\hat{a}_j\hat{a}^\dagger_k\hat{a}_k\hat{a}^\dagger_m\hat{a}_l|\Psi\rangle = {}^3\tilde{E}^{ijk}_{lmk}, \tag{15}$$

$$\langle\Phi^G_{ij}|\hat{a}_k\hat{a}^\dagger_k|\Phi^G_{lm}\rangle = \langle\Psi|\hat{a}^\dagger_i\hat{a}_j\hat{a}_k\hat{a}^\dagger_k\hat{a}^\dagger_m\hat{a}_l|\Psi\rangle = {}^3\tilde{F}^{ijk}_{lmk}, \tag{16}$$

$$\langle\Phi^Q_{ij}|\hat{a}^\dagger_k\hat{a}_k|\Phi^Q_{lm}\rangle = \langle\Psi|\hat{a}_i\hat{a}_j\hat{a}^\dagger_k\hat{a}_k\hat{a}^\dagger_m\hat{a}^\dagger_l|\Psi\rangle = {}^3F^{ijk}_{lmk}, \tag{17}$$

$$\langle\Phi^Q_{ij}|\hat{a}_k\hat{a}^\dagger_k|\Phi^Q_{lm}\rangle = \langle\Psi|\hat{a}_i\hat{a}_j\hat{a}_k\hat{a}^\dagger_k\hat{a}^\dagger_m\hat{a}^\dagger_l|\Psi\rangle = {}^3Q^{ijk}_{lmk}. \tag{18}$$

Three distinct sets of linear mappings for the partial 3-positivity matrices in Eqs. (13)–(18) are important: (i) the contraction mappings which relate the lifted metric matrices

to the 2-positive matrices in Eqs. (5)–(7), (ii) the linear interconversion mappings from rearranging creation and annihilation operators to interrelate the lifted metric matrices, and (iii) antisymmetry (or symmetry) conditions which enforce the permutation of the creation operators for fermions (or bosons). Note that the correct permutation of the annihilation operators is automatically enforced from the permutation of the creation operators in (iii) by the Hermiticity of the matrices.

C. Comparison with T_1 and T_2

Addition of any two positive semidefinite matrices produces a positive semidefinite matrix. Hence the four 3-positivity conditions [8] imply the following two less stringent conditions:

$$T_1 = {}^3D + {}^3Q \geqslant 0, \tag{19}$$

$$T_2 = {}^3E + {}^3F \geqslant 0, \tag{20}$$

which were originally proposed by Erdahl [6] and recently implemented for small atoms and molecules by Zhao *et al.* [18]. 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 [9,23–29] for the 3-particle and 3-hole RDMs

$${}^3D/6 = {}^1D \wedge {}^1D \wedge {}^1D + 3({}^2D/2 - {}^1D \wedge {}^1D) \wedge {}^1D + {}^3\Delta \tag{21}$$

and

$${}^3Q/6 = {}^1Q \wedge {}^1Q \wedge {}^1Q + 3({}^2Q/2 - {}^1Q \wedge {}^1Q) \wedge {}^1Q - {}^3\Delta \tag{22}$$

where the wedge $\wedge$ denotes the antisymmetric tensor product, known as the Grassmann wedge product [30], 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 [9], and hence the T_1 matrix depends only upon the 2-particle RDM. Similarly, because the elements of the T_2 matrix can be expressed as

$$(T_2)^{ijk}_{lmn} = ({}^2D^{ij}_{lm} + {}^2Q^{lm}_{ij})\delta^k_n - ({}^3D^{ijn}_{lmk} + {}^3Q^{ijn}_{lmk}), \tag{23}$$

it follows that the connected parts of the 3-RDM again cancel in the addition of ${}^3D$ and ${}^3Q$. For bosons restricting the T_1 and the T_2 matrices to be positive semidefinite also enforces a subset of 3-positivity, but because bosons exchange symmetrically, these matrices still depend upon the 3-RDM.

III. APPLICATIONS

A. Summary of *N*-representability conditions

In variational density matrix theory the energy is minimized with respect to a 2-RDM restricted by necessary *N*-representability conditions. Each representation of the reduced density matrices is constrained to be (i) Hermitian, (ii) normalized, (iii) positive semidefinite, and (iv) antisymmetric (fermions) or symmetric (bosons) in particle exchange. For example, with 2-positivity there are three metric-matrix representations of the 2-RDM, ${}^2D$, ${}^2Q$, and ${}^2G$, that are constrained to satisfy these four conditions. Furthermore, each representation must be consistent with the other matrix representations according to the linear mappings generated from either contracting or rearranging the creation and annihilation operators.

B. Description of the model

The Lipkin model [31] is a soluble, two-level quasispin system with two-body interactions, which has proven useful for evaluating computational methods [8,9,23,32–39]. The model demonstrates the breakdown of perturbative methods at large correlation as well as the size-consistency errors of truncated CI methods [8]. The Lipkin model for N spin-1/2 particles consists of two distinct levels denoted by the quantum number $m = \pm 1$ where each level contains N states denoted by the quantum number p. Only one of the N spin fermions can occupy each of the $2N$ states. When interpreted according to the states, the Lipkin model describes a quantum system of N spin-1/2 fermions. In second quantization the Hamiltonian for the Lipkin model is given by

$$\hat{H} = \frac{\epsilon}{N}\sum_{m=\pm1,p} m\hat{a}^\dagger_{m,p}\hat{a}_{m,p} + \frac{V}{N(N-1)}\sum_{m=\pm1,p_1,p_2}\hat{a}^\dagger_{+m,p_1}\hat{a}^\dagger_{+m,p_2}\hat{a}_{-m,p_2}\hat{a}_{-m,p_1} \tag{24}$$

where the parameter ϵ controls the weight of the one-particle number operator and the parameter V controls the weight of the interaction which is minimized when the spins are equally distributed between the two energy levels. However, because N particles can occupy each level, the Lipkin model may also be interpreted as a two-level bosonic system. The Hamiltonian for the boson formulation of the Lipkin model may be written as

$$\hat{H} = \frac{\epsilon}{N}\sum_{m=\pm1} m\hat{b}^\dagger_m\hat{b}_m + \frac{V}{N(N-1)}\sum_{m=\pm1}\hat{b}^\dagger_{+m}\hat{b}^\dagger_{+m}\hat{b}_{-m}\hat{b}_{-m}, \tag{25}$$

where $\hat{b}^\dagger_i$ and $\hat{b}_j$ are the bosonic creation and annihilation operators which obey the commutation relations $[b_j, b^\dagger_i] = \delta^i_j$ and $[b_j, b_i] = 0$. Because the Hamiltonians in Eqs. (24) and (25) represent the same physical system, they have the same ground-state energies and wave functions where the boson wave functions are more compact since they directly include the indistinguishability of the p states. Within the fermionic interpretation the 2-RDM scales as $2N^2$. To avoid this scaling by incorporating symmetry of the p-states within the RDMs, we represent the RDMs with the boson creation and annhilation operators. For example, with the boson operators the D, Q, and G matrices are

$$D^{i,j}_{k,l} = \langle\psi|b^\dagger_i b^\dagger_j b_l b_k|\psi\rangle, \tag{26}$$

TABLE I. Comparison of RDM methods to wave-function methods as a means for calculating correlation energy in the Lipkin model [31]. Configuration interaction, many-body perturbation theory, and coupled-cluster singles-doubles are compared to 2-positivity, 3-positivity and two variants of partial 3-positivity discussed in the text. The correlation parameter is $V=0.99$. Numbers in square brackets denote powers of ten.

		Percentage of correlation energy							
		Wave-function methods				RDM methods			
N	FCI correlation energy	CISD	CISDTQ	MP2	CCSD	2-Pos	T_1/T_2	Lifting	3-Pos
10	−6.1214[−2]	79.32	97.46	88.95	103.03	108.47	108.47	107.56	100.15
25	−2.6397[−2]	69.41	91.02	77.35	105.39	107.36	107.36	106.77	100.13
50	−1.4012[−2]	64.16	86.04	71.37	106.17	106.33	106.33	105.93	100.10
75	−9.6456[−3]	61.76	83.43	68.66	106.23	105.69	105.69	105.38	100.15
100	−7.3874[−3]	60.29	81.76	67.01	106.12	105.24	105.23	104.98	100.07

$$Q^{i,j}_{k,l} = \langle \psi | b_i b_j b_l^\dagger b_k^\dagger | \psi \rangle, \tag{27}$$

and

$$G^{i,j}_{k,l} = \langle \psi | b_i^\dagger b_j b_l^\dagger b_k | \psi \rangle. \tag{28}$$

Similar expressions are readily constructed for the metric matrices of partial and full 3-positivity. A more detailed description of the Lipkin model is available in the literature [8,9,23,32–35].

C. Computational details

Minimizing the energy as a functional of the 2-RDM subject to the 2-positivity conditions requires the solution of an optimization problem known as a semidefinite program. We solve the program using the *primal-dual interior-point algorithm* implemented in the program SeDuMi [40]. The primal form of the algorithm is stated as

$$\text{minimize } \langle c|x\rangle$$

$$\text{such that } A|x\rangle = |b\rangle,$$

$$M(x) \geqslant 0, \tag{29}$$

where $\langle c|$ contains information about the unconstrained system, which for this specific application includes the matrix elements of the reduced Hamiltonian ${}^2K$. The vector $|x\rangle$ contains the elements of the matrices ${}^2D$, ${}^2Q$, and ${}^2G$, as well as the lifted matrices or the 3-positive matrices, such that $\langle c|x\rangle$ corresponds to $\mathrm{Tr}[{}^2K{}^2D]$ and the $m\times n$ constraint matrix A in $A|x\rangle - |b\rangle = 0$, where m and n are the number of constraints and number of elements in $|x\rangle$, respectively, enforces the trace, antisymmetry (or symmetry in the boson formulation), and contraction conditions, as well as the linear mappings which relate different representations of the 2-RDM and the lifted matrix. $M(x)$ is a block-diagonal matrix containing in each block one representation of the 2-RDM that is being constrained to be positive semidefinite. Holding the matrix M positive semidefinite constrains all the necessary matrices to be positive semidefinite.

D. Results

The ground-state energies and 2-RDMs of the Lipkin spin model are determined by variational 2-RDM methods using different N-representability conditions including the 2-positivity conditions, two types of partial 3-positivity conditions, the lifting [Eqs. (13)–(18)] and the T_1/T_2 constraints, as well as the complete 3-positivity conditions. In Eq. (24) we set $\epsilon=1$ and $V=0.99$ to make the interaction strength V slightly less than the absolute value of the one-particle energy ϵ. These results are compared to the energies and 2-RDMs from full configuration interaction (FCI) [9] and approximate wave-function methods including configuration interaction with single and double excitations (CISD) [8], configuration interaction with single, double, triple, and quadruple excitations (CISDTQ) [8], second-order many-body perturbation theory (MP2), and coupled cluster with single-double excitations (CCSD) [8,39].

In Table I the percentages of the recovered correlation energy (CE) are presented for the number N of spins ranging from 10 to 100. Because the N-representability conditions are necessary but not sufficient, the correlation energies from the variational 2-RDM methods are *lower bounds* to the FCI results. The 2-RDM method with 2-positivity conditions yields between 108.47% and 105.24% of the CE for N between 10 and 100. The lifting conditions improve the results to 107.56% and 104.98% for N equal to 10 and 100, respectively, while the T_1 and T_2 conditions do not exhibit any improvement. Full 3-positivity provides a dramatic increase in accuracy with recovery of 100.15% and 100.07% of the CE at $N=10$ and 100. At $N=50$ the approximate wave-function methods, CISD, CISDTQ, MP2, and CCSD, capture 64.16%, 86.04%, 71.37%, and 106.17% of the CE, respectively. The CCSD method, yielding the most accurate energies of the approximate wave-function techniques, gives slightly better correlation energies at low N and slightly worse energies at high N than the 2-RDM method with 2-positivity or lifting conditions. In contrast to the 2-RDM methods which improve as N increases, each of the approximate wave-function methods becomes less accurate with increasing N. The 2-RDM method with 3-positivity produces energies that are better by one-and-a-half to three orders-of-

TABLE II. Comparison of natural orbital and natural geminal occupation numbers (density matrix eigenvalues) for different levels of theory, including configuration interaction and the positivity methods discussed in the text. The parameters are $N=10$, $V=0.99$.

		Occupation numbers					
Matrix	Orbital/geminal	FCI	CISD	2-Pos	T_1/T_2	Lifting	3-Pos
^1D	ϕ_0	0.9625	0.9023	0.9520	0.9520	0.9535	0.9622
	ϕ_1	0.03750	0.09768	0.04802	0.04804	0.04653	0.03784
^2D	g_1	0.9364	1.0000	0.9187	0.9187	0.9211	0.9358
	g_2	0.06235	0.00000	0.08127	0.08130	0.07887	0.06304
	g_3	0.001235	0.000000	0.000000	0.000000	0.000048	0.001172

magnitude than those from either 2-positivity or CCSD.

The eigenfunctions of the 1- and 2-RDMs are known as the natural orbitals $\phi_i(1)$ and natural geminals $g_i(1,2)$, respectively. In Table II for the Lipkin model with $N=10$ we present for the ground state the occupation numbers of the natural orbitals and geminals from variational 2-RDM methods with different levels of N-representability as well as from the wave-function methods CISD and FCI. The sums of the occupation numbers for the 1-RDM and the 2-RDM are normalized to one. Note that as many as N spin fermions can occupy a given natural orbital such as ϕ_1 because there are actually N orbitals ϕ_1 that are distinguished by the quantum number p in the Lipkin Hamiltonian in Eq. (24). The lifting conditions provide consistent improvement of the occupation numbers from the 2-positivity values towards the FCI values. The occupation numbers from each of the 2-RDM methods are significantly more realistic than the occupation numbers from CISD. The 2-RDM method with 3-positivity reproduces the occupation numbers of the natural orbitals and geminals to an accuracy on the order of 10^{-4}.

IV. DISCUSSION AND CONCLUSIONS

The variational calculation of the 2-RDM without the many-electron wave function has been performed for a variety of atoms and molecules in minimal basis sets [5,10–14,18,19], and recently, the variational 2-RDM method has been applied to larger molecules and basis sets through the development of a first-order algorithm for semidefinite programming [19–21]. There exists a systematic hierarchy of N-representability conditions, known as p-positivity conditions, which enforce the generalized uncertainty relations for all pairs of $p/2$-body operators [8]. Each of the recent variational 2-RDM calculations has employed the 2-positivity conditions, but only two previous calculations on atoms and molecules have explored higher positivity conditions [12,18]. The variational calculations with 2-positivity have been shown to treat single- and multireference correlation effects with similar accuracy which permits the generation of realistic potential energy surfaces [12–14,16,19–21]. While calculations of potential energy curves and organic molecules with different functional groups also reveal some correlation effects within molecules that are not captured with sufficient chemical accuracy by 2-positivity, the addition of complete 3-positivity conditions within molecular calculations is computationally expensive. Two different *partial 3-positivity* conditions, therefore, have been proposed: (i) the lifting conditions of Mazziotti and (ii) the T_1/T_2 conditions of Erdahl [6] implemented by Zhao *et al.* [18]. In Mazziotti [12] the lifting conditions were applied to boron hydride (BH), but their formulation required manipulation and storage of the 3-RDM. The present paper develops a variational RDM method with lifting conditions that incorporates these conditions without the complete 3-RDM. The lifting conditions are compared theoretically with the T_1/T_2 conditions of Erdahl, and both of these partial 3-positivity conditions are implemented for a Lipkin spin model where they are compared with 2- and 3-positivity as well as with approximate wave-function methods.

The six lifting conditions for partial 3-positivity arise from inserting one-particle and one-hole projection operators into the D-, Q-, and G-matrices within 2-positivity. Because many-electron Hamiltonians contain only pairwise interactions, an important subset of 3-positivity conditions should be the constraints that map or "lift" the metric matrices of 2-positivity to the three-particle space specifically to target quantum systems with pairwise interactions. In contrast to the lifting conditions each of the T_1 and T_2 conditions arises from constraining a sum of two 3-positive metric matrices to be positive semidefinite as shown in Eqs. (19) and (20). These sums of the 3-positive metric matrices cause the T_1 and T_2 conditions to depend only upon the 2-RDM. Using the cumulant expansions of the 3-particle and 3-hole RDMs [9,23–29], we show that their addition to form the T_1 condition causes the *cumulant* or *connected* parts of the 3-particle and 3-hole RDMs to cancel. Within cumulant theory the connected part of an RDM is the portion that cannot be written as wedge products of lower RDMs. In the literature on the contracted Schrödinger equation [9,13,41,42] it has been shown that the connected part of the 3-hole RDM equals the negative of the connected part of the 3-particle RDM [9,23–29], and hence upon addition in the T_1 condition they cancel, and we obtain a formula that depends only upon the lower 1- and 2-RDMs. A similar analysis holds for the T_2 condition. The recent introduction of a first-order semidefinite programming algorithm for the 2-RDM variational method with 2-positivity conditions reduced the scaling of the method by orders of magnitude from r^{16} [43] to r^6 where r is the number of spatial orbitals in the basis set [19,20]. In the context of a similar first-order algorithm for atoms and

molecules the lifting conditions would scale computationally as r^7 while the T_1 and T_2 conditions would scale as r^9. The scaling of the T_1 and T_2 conditions within the 2-RDM method is presently similar to 3-positivity, but further reduction in the scaling may be possible.

In an application to the Lipkin spin model the variational 2-RDM method with partial 3-positivity conditions is compared to the 2-RDM methods with 2- and 3-positivity conditions as well as approximate wave-function techniques. For the number of particles ranging from 10 to 100 fermions and a strong interaction strength of $V=0.99$ the 2-RDM method with 2-positivity overestimates the correlation energy by 5–9% while with 3-positivity the method overestimates the correlation energy by a maximum of only 0.15%. For the Lipkin model the T_1 and T_2 conditions do not improve the correlation energy. In contrast, for atoms and molecules in minimal basis sets the T_2 condition corrects the correlation energy of 2-positivity by one or two orders of magnitude to produce energy errors largely between 0.1 and 0.001 millihartrees [18]. Because the positivity conditions correct the energies exactly for certain classes of Hamiltonians and interactions regardless of the strength of the perturbation [16,17,20], the strength of the conditions depends importantly upon the nature of the interaction. The computational results indicate that the T_2 condition restricts a class of Hamiltonians that is more appropriate for treating the two-electron Coulomb interactions in atoms and molecules than the spin-spin interactions of the Lipkin model. The partial 3-positivity conditions known as the lifting conditions, however, reduce the overestimation of the correlation energy by as much as 1%. These results show that the lifting conditions without storing the 3-RDM contain nontrivial N-representability conditions that are not contained in the 2-positivity constraints. The calculations with the Lipkin model demonstrate that the lifting conditions can be more stringent than the T_1 and T_2 conditions. Although it is not possible to draw conclusions from these calculations about their performance for atoms and molecules, the dramatic improvement of molecular correlation energies from the T_2 condition suggests that a similar or better improvement may be observed from the lifting conditions.

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