

Purification of correlated reduced density matrices

David A. Mazziotti

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

(Received 3 August 2001; published 18 January 2002)

The notion of purification is generalized to treat correlated reduced density matrices. Traditionally, purification denotes the process by which a one-particle reduced density matrix (1-RDM) is made idempotent, that is, its eigenvalues are mapped to either 0 or 1. Purification of correlated RDMs is defined as the iterative process by which an arbitrary RDM is forced to satisfy several necessary N -representability conditions. Using the unitary decomposition of RDMs and the positivity conditions, we develop an algorithm to purify the 2-RDM. The algorithm is applied within the solution of the contracted Schrödinger equation CSE for the 2-RDM [D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998)]. Previous attempts to solve the CSE by powerlike methods have frequently produced divergent energies, but we show that the purification process eliminates the divergent behavior for systematic and reliable convergence of the contracted power method to the N -particle energy.

DOI: 10.1103/PhysRevE.65.026704

PACS number(s): 02.70.-c, 31.15.Ew, 31.10.+z, 31.25.-v

I. INTRODUCTION

The two-particle reduced density matrix (2-RDM) for atoms and molecules has recently been computed directly without the wave function through the 2,4-contracted Schrödinger equation (CSE) and density-matrix reconstruction [1–19]. The CSE is a contraction of the N -electron Schrödinger equation onto the space of two quasidelectrons. While the CSE contains not only the 2-RDM but also the 3- and the 4-RDMs, a strategy for solving the CSE has been developed by reconstructing the 3- and the 4-RDMs from the 2-RDM through cumulant theory. Application of the CSE with density-matrix reconstruction has yielded the correlation energies for a variety of systems from atoms and molecules to spin models and random Hamiltonians.

From these calculations two general strategies have emerged for the solution of the CSE after reconstruction: (i) self-consistent iteration [2–9] and (ii) Newton's method for nonlinear equations [5,6,19]. For BeH₂ Valdemoro, Tel, and Perez-Romero obtained good convergence of the CSE with self-consistent iteration [4], but Yasuda and Nakatsuji found that a self-consistent strategy often produced divergence of the CSE and its energy [6]. Hence, Yasuda and Nakatsuji performed their calculations with a Newton's method, which, however, is more expensive and not without convergence issues [5,6,19]. We showed that the self-consistent iteration of the CSE could be connected with the power method for eigenvalues, and we employed a contracted power method to solve the CSE for Lipkin's quasispin model. After examining various approaches for the CSE's solution, we recently designed a contracted power method that exhibits consistent and reliable convergence to the N -particle solution [20]. The success of the contracted power method depends upon the purification of *correlated* RDMs that will be developed in this paper.

The concept of purification is well known in the linear-scaling literature where it denotes the iterative process by which an arbitrary one-particle density matrix is projected onto an idempotent 1-RDM [21–24]. An RDM is said to be *pure* N representable if it arises from the integration of an

N -particle density matrix $\Psi\Psi^*$, where Ψ (the preimage) is an N -particle wave function [18,25,26]. Any idempotent 1-RDM is N representable with a unique Slater-determinant preimage. Within the linear-scaling literature the 1-RDM may be directly computed with unconstrained optimization where iterative purification imposes the N -representability conditions [22–24]. Recently, we have shown that these methods for computing the 1-RDM directly are related to the solution of the 1,2-CSE by a contracted power method (1,2-CSE is the contraction of the Schrödinger equation onto the one-particle space) [27]. While purification for noninteracting 1-RDMs was first pioneered by McWeeny in the late 1950s [21], the concept has not been previously extended to correlated density matrices. We define *purification of correlated* RDMs as the iterative process by which an arbitrary p -particle density matrix is projected onto a p -RDM, which obeys several necessary conditions for N representability. Note that the word *necessary* is used since the full set of N -representability conditions for the p -RDM ($p > 1$) is not known. Although there is considerable literature on minimizing the energy with respect to a 2-RDM, which is constrained by N -representability conditions [17,18,25,26,28–33], the literature on correcting a 2-RDM, which is not N representable, is not large [4,14,34,35]. The need for such techniques is suggested by the iterative nature of the CSE. The extension of purification to the 2-RDM plays a role in the solution of the 2,4-CSE, which is analogous to the role of 1-RDM purification in the solution of the 1,2-CSE.

McWeeny's purification of the 1-RDM may be derived with calculus or polynomial theory [27,36,37], but the development of purification methods for correlated RDMs requires different machinery including the unitary decomposition of RDMs [38–44], cumulant reconstruction of RDMs [8,9,12,15,19,45], and the known 2-RDM positivity conditions for N representability [17,46]. These concepts will be reviewed as we develop an iterative algorithm for purifying correlated RDMs. The final method is illustrated by purifying a non- N -representable two-particle density matrix that was obtained as an intermediate during a CSE calculation on H₂O, and then we show that purification after each iteration of the CSE dramatically improves the convergence of the contracted power method.

II. THEORY

Purification of the 2-RDM begins with checking that the 2-RDM contracts to a 1-RDM, which is N representable. After the 1-RDM is adjusted as shown in Sec. II A, the corresponding 2-RDM may be updated through the unitary decomposition from Sec. II B. The 1-RDM determines through the unitary and cumulant decompositions different parts of the 2-RDM. In Sec. II D the remaining, two-particle portion of the 2-RDM is purified through positivity conditions for the 2-RDM. Special considerations for purifying a 2-RDM with spin are discussed within the final section.

A. N representability of the 1-RDM

Some of the most important N -representability conditions on the 2-RDM arise from its relationship with the 1-RDM. A 2-RDM must contract to a 1-RDM that is N representable,

$${}^1D = \left(\frac{2}{N-1} \right) L_2^1({}^2D). \quad (1)$$

The operator L_2^1 , defined in the Appendix, denotes the contraction operator that maps the 2-RDM to the 1-RDM. The factor of $(N-1)/2$ arises from the normalization of the 1-RDM and 2-RDM to N and $N(N-1)/2$, respectively. The N -representability conditions for the 1-RDM arise from the *particle-hole duality* [17,47,48]. The expectation value of the anticommutation relation for fermions,

$$a_j a_i^\dagger + a_i^\dagger a_j = \delta_j^i, \quad (2)$$

yields the relation between the elements of the 1-RDM, ${}^1D_j^i$, and the elements of the one-hole RDM, ${}^1\bar{D}_j^i$,

$${}^1\bar{D}_j^i + {}^1D_j^i = {}^1I_j^i, \quad (3)$$

where 1I is the identity matrix. Any 1-RDM is ensemble N representable if and only if it is Hermitian with trace N and both the 1-RDM and one-hole RDM are positive semidefinite [17,18,25,47,48], which is denoted by

$${}^1D \geq 0 \quad (4)$$

and

$${}^1\bar{D} \geq 0. \quad (5)$$

A matrix is *positive semidefinite* if and only if all of its eigenvalues are non-negative. Because the 1-RDM and the one-hole RDM share the same eigenvectors, these two positivity restrictions are equivalent to constraining the occupation numbers of the 1-RDM to lie between 0 and 1 [25].

Purification of a trial 2-RDM with the 1-RDM conditions may be accomplished by contracting the 2-RDM as in Eq. (1) and checking that the eigenvalues of the 1-RDM lie between 0 and 1. If the eigenvalues fall outside this interval, neither the 1-RDM nor the 2-RDM can be N representable. Any method for adjusting the 1-RDM occupation numbers must preserve the trace of the 1-RDM, which is the number N of particles. We have employed the following algorithm to

effect this purification: (i) set all of the negative 1-RDM eigenvalues to zero, (ii) correct the trace by decreasing the occupation number for the highest occupied orbital, (iii) set to 1 all 1-RDM eigenvalues that are greater than 1, and (iv) correct the trace by increasing the occupation number for the lowest unoccupied orbital. We decrease the highest occupied orbital and increase the lowest unoccupied orbital since these changes are unlikely to produce occupation numbers outside the $[0,1]$ interval. This is only one reasonable approach to ensuring that the occupation numbers of the 1-RDM are N representable; many variations on this simple strategy may also be employed. Once the 1-RDM has been adjusted to be N representable, we need a method for modifying the 2-RDM so that it contracts by Eq. (1) to the updated 1-RDM. The appropriate modification of the 2-RDM may be accomplished through the unitary decomposition of the 2-RDM, which we discuss in the following section.

B. Unitary decomposition of the 2-RDM

Any two-particle Hermitian matrix 2A may be decomposed into three components that exist in different subspaces of the unitary group. These components reveal the structure of the matrix with respect to the contraction operation [18,38–42]

$${}^2A = {}^2A_0 + {}^2A_1 + {}^2A_2, \quad (6)$$

where

$${}^2A_0 = \frac{2 \operatorname{Tr}({}^2A)}{r(r-1)} {}^2I, \quad (7)$$

$${}^2A_1 = \frac{4}{r-2} {}^1A \wedge {}^1I - \frac{4 \operatorname{Tr}({}^2A)}{r(r-2)} {}^2I, \quad (8)$$

and

$${}^2A_2 = {}^2A - \frac{4}{r-2} {}^1A \wedge {}^1I + \frac{2 \operatorname{Tr}({}^2A)}{(r-1)(r-2)} {}^2I. \quad (9)$$

The one-particle matrix 1A is the contraction of the two-particle matrix 2A ,

$${}^1A = L_2^1({}^2A), \quad (10)$$

the symbol r denotes the rank of the one-particle basis set, the wedge product \wedge is defined in the Appendix, and

$${}^2I = {}^1I \wedge {}^1I. \quad (11)$$

The zeroth component 2A_0 contains the trace information for 2A ,

$$L_2^0({}^2A_0) = \operatorname{Tr}({}^2A_0) = \operatorname{Tr}({}^2A), \quad (12)$$

and the first component 2A_1 contains the one-particle information for 2A except for the trace

$$L_2^1({}^2A_0 + {}^2A_1) = {}^1A. \quad (13)$$

The two-particle component of 2A carries information that vanishes upon contraction,

$$L_2^1({}^2A_2) = 0, \quad (14)$$

where 0 in this equation represents the zero matrix.

The unitary decomposition may be applied to any Hermitian, antisymmetric two-particle matrix including the 2-RDM, the two-hole RDM, and the two-particle reduced Hamiltonian. The decomposition is also readily generalized to treat p -particle matrices [42–44]. The trial 2-RDM to be purified may be written as

$${}^2D = {}^2D_0 + {}^2D_1 + {}^2D_2. \quad (15)$$

Note that if ${}^2A = {}^2D$ in Eqs. (7), (8), and (9), then from Eqs. (1) and (13) we have that

$${}^1A = \left(\frac{N-1}{2} \right) {}^1D. \quad (16)$$

Using Eq. (8) and the adjusted 1-RDM from the preceding section, we can construct a modified one-particle portion of the 2-RDM ${}^2D_1^a$. Then the appropriate 2-RDM that contracts to the adjusted 1-RDM is readily expressed as

$${}^2D^a = {}^2D_0 + {}^2D_1^a + {}^2D_2. \quad (17)$$

Both the trace and one-particle subspaces of the 2-RDM are now N representable. Does the 1-RDM tell us anything about the two-particle component of the 2-RDM that vanishes when it is contracted to the one-particle space? Before examining additional N -representability conditions, we address this question in the following section.

C. Cumulant decomposition of the 2-RDM

The unitary decomposition is not the only approach for expressing the RDMs in terms of lower RDMs. Recently, in the context of the CSE, the 3- and the 4-RDMs have been reconstructed from the 2-RDM through particle-hole duality [1,2], the Green's function theory [5,6], and the cumulant theory [8,9,12,15,19,45]. Each of these approaches yields the same decomposition for the 2-RDM,

$${}^2D = {}^1D \wedge {}^1D + {}^2\Delta, \quad (18)$$

where the elements of the 2-RDM are

$${}^2D_{k,l}^{i,j} = \frac{1}{2} \langle \Psi | a_i^\dagger a_j^\dagger a_l a_k | \Psi \rangle. \quad (19)$$

The portion of the 2-RDM that may be expressed as a wedge product of lower RDMs is said to be *unconnected*. The unconnected portion of the 2-RDM contains an important portion of the two-particle component from the unitary decomposition 2D_2 , and similarly, the trace and one-particle unitary components contain an important portion of the connected 2-RDM ${}^2\Delta$, which corrects the contraction. Both decompositions may be synthesized by examining the unitary decomposition of the connected 2-RDM,

$${}^2\Delta = {}^2\Delta_0 + {}^2\Delta_1 + {}^2\Delta_2. \quad (20)$$

The trace and the one-particle components of the connected 2-RDM are completely determined by the 1-RDM. Hence, it is *the two-particle unitary subspace of the connected 2-RDM that may require further purification*.

Similarly, the cumulant decomposition for the two-hole RDM is

$${}^2\bar{D} = {}^1\bar{D} \wedge {}^1\bar{D} + {}^2\bar{\Delta}, \quad (21)$$

where the elements of the two-hole RDM are

$${}^2\bar{D}_{k,l}^{i,j} = \frac{1}{2} \langle \Psi | a_l a_k a_i^\dagger a_j^\dagger | \Psi \rangle. \quad (22)$$

With the anticommutation relation for fermions in Eq. (2) and the second-quantized definitions, it has been shown that the connected portions of the two-particle and two-hole RDMs are equal [1,7,49],

$${}^2\bar{\Delta} = {}^2\Delta \quad (23)$$

It follows forthwith that

$${}^2\bar{\Delta}_2 = {}^2\Delta_2. \quad (24)$$

Therefore, we have the important fact that *for a fixed 1-RDM any correction to the 2-RDM will also be a correction to the two-hole RDM*. In the following section we use this fact in purifying the 2-RDM to satisfy two N -representability restrictions.

D. N representability of the 2-RDM

Two significant N -representability conditions on the 2-RDM are that both the two-particle and the two-hole RDMs must be positive semidefinite,

$${}^2D \geq 0 \quad (25)$$

and

$${}^2\bar{D} \geq 0. \quad (26)$$

In the N -representability literature these positivity conditions are known as the D and the Q conditions [17,26,46,48]. More details on positivity may be found in Ref. [17], where the concept of positivity and its connection to the generalized uncertainty relations is developed. The two-particle RDM and the two-hole RDM are linearly related via the particle-hole duality

$${}^2\bar{D} = {}^2I - 2 {}^1D \wedge {}^1I + {}^2D. \quad (27)$$

If the trial 2-RDM does not obey the D condition, then it has a set of eigenvectors $\{v_i\}$ whose associated eigenvalues are negative. Hence, we can construct a set of two-particle matrices $\{{}^2O_i\}$

$${}^2O_i = v_i v_i^\dagger, \quad (28)$$

for which

$$\text{Tr}({}^2O_i {}^2D) < 0. \quad (29)$$

Each member of the set $\{^2O_i\}$ is said to *expose* the 2-RDM [18,50]. Similarly, if the trial 2-RDM does not obey the Q condition, then the two-hole RDM has a set of eigenvectors $\{\bar{v}_i\}$ whose associated eigenvalues are negative. The bar in \bar{v}_i simply distinguishes the eigenvectors of the two-hole RDM from those of the 2-RDM; it does not denote the adjoint. A set of two-hole matrices $\{^2\bar{O}_i\}$ may be generated,

$$^2\bar{O}_i = \bar{v}_i \bar{v}_i^\dagger, \quad (30)$$

for which

$$\text{Tr}(^2\bar{O}_i ^2\bar{D}) < 0. \quad (31)$$

As with the D condition, each member of the set $\{^2\bar{O}_i\}$ is said to expose the two-hole RDM.

The 2-RDM may be made positive semidefinite if each of the negative eigenvalues is set to zero, but this alters not only the positivity but also the contraction of the 2-RDM to the 1-RDM and even the 2-RDM trace. How can we modify the 2-RDM to prevent it from being exposed by the set $\{^2O_i\}$ and yet maintain contraction to the N -representable 1-RDM? Again we can employ the unitary decomposition. For a matrix 2O_i the decomposition is

$$^2O_i = ^2O_{i;0} + ^2O_{i;1} + ^2O_{i;2}. \quad (32)$$

Making the 2-RDM eigenvalue associated with v_i equal to zero is equivalent to adding an appropriate amount of 2O_i to the 2-RDM. However, this also changes the trace and the underlying 2-RDM because 2O_i contains the zeroth and the first components of the unitary decomposition. We can modify the two-particle component only by adding just $^2O_{i;2}$ rather than 2O_i . The adjusted 2-RDM may then be expressed as

$$^2D_a = ^2D + \sum_i \alpha_i ^2O_{i;2}, \quad (33)$$

where the set of coefficients is determined from the system of linear equations

$$\text{Tr}(^2O_i ^2D_a) = 0 \quad \forall i. \quad (34)$$

Although the adjusted 2-RDM is not exposed by any of the matrices in the set $\{^2O_i\}$, in general, there will be new eigenvectors with negative eigenvalues. However, these negative eigenvalues are, in general, smaller than those of the unadjusted 2-RDM. Hence, by repeating this process *iteratively*, the 2-RDM may be purified so that the D condition is satisfied *without* modifying the contraction.

Analogously, the two-hole matrices in the set $\{^2\bar{O}_i\}$ may be decomposed,

$$^2\bar{O}_i = ^2\bar{O}_{i;0} + ^2\bar{O}_{i;1} + ^2\bar{O}_{i;2}. \quad (35)$$

To impose only the Q condition, we have an adjusted two-hole RDM

$$^2\bar{D}_a = ^2\bar{D} + \sum_i \beta_i ^2\bar{O}_{i;2}, \quad (36)$$

whose coefficients are determined from the system of linear equations

$$\text{Tr}(^2\bar{O}_i ^2\bar{D}_a) = 0 \quad \forall i. \quad (37)$$

One possibility for imposing both the D and the Q conditions is to update the 2-RDM via Eqs. (33) and (34), convert the 2-RDM to the two-hole RDM, update the two-hole RDM via Eqs. (36) and (37), and then to repeat this process until convergence. However, this alternating approach does not usually show good convergence since the 2-RDM changes often damage Q positivity and the two-hole RDM changes often adversely affect D positivity. A better approach would be to impose both the D and the Q updates *simultaneously*.

A simultaneous purification with respect to both the D and the Q conditions may be achieved by using the fact that for a fixed 1-RDM any correction to the 2-RDM will also be a correction to the two-hole RDM and vice versa. This suggests that we write the adjusted 2-RDM as

$$^2D_a = ^2D + \sum_i \alpha_i ^2O_{i;2} + \sum_i \beta_i ^2\bar{O}_{i;2}, \quad (38)$$

where the expansion coefficients are determined by solving the linear equations in both Eqs. (34) and (37) simultaneously. Note that the linear mapping between the 2-RDM and the two-hole RDM must be employed in Eq. (37). The resulting adjusted 2-RDM will not be exposed by either the operators $\{^2O_i\}$ or, in its two-hole form, the operators $\{^2\bar{O}_i\}$. Repeated application of this purification produces a 2-RDM that satisfies, to a specified tolerance, the D and Q conditions.

E. Spin of the 2-RDM

The RDMs for atoms and molecules have a special structure from the spin of the electrons. To each spatial orbital, we associate a spin of either α or β . Because the two spins are orthogonal upon integration of the N -particle density matrix, only RDM blocks where the net spin of the upper indices equals the net spin of the lower indices do not vanish. Hence, a p -RDM is block diagonal with $(p+1)$ nonzero blocks. Specifically, the 1-RDM has two nonzero blocks, an α block and a β block,

$$^1D_{\alpha,j}^{\alpha,i} \neq 0, \quad ^1D_{\beta,j}^{\beta,i} \neq 0, \quad (39)$$

and the 2-RDM has three nonzero blocks, an α/α block, an α/β block, and a β/β block,

$$^2D_{\alpha,j;\alpha,l}^{\alpha,i;\alpha,k} \neq 0, \quad ^2D_{\alpha,j;\beta,l}^{\alpha,i;\beta,k} \neq 0, \quad ^2D_{\beta,j;\beta,l}^{\beta,i;\beta,k} \neq 0. \quad (40)$$

The spin structure enhances computational efficiency since each of the blocks may be purified separately.

For the remainder of this section we treat closed-shell atoms and molecules where the α and the β spins are indistinguishable. Because the α and the β blocks of the 1-RDM

are equal, we need only purify the eigenvalues for one of these blocks. As in Sec. II A the eigenvalues of the 1-RDM must lie in the interval $[0,1]$ with the trace of each block equal to $N/2$. Similarly, with the α/α and the β/β blocks of the 2-RDM being equal, only one of these blocks requires purification. The purification of either block is the same as in Sec. II D with the normalization being $N(N/2-1)/4$. The unitary decomposition ensures that the α/α block of the 2-RDM contracts to the α component of the 1-RDM. The purification of Sec. II D, however, cannot be directly applied to the α/β block of the 2-RDM since the spatial orbitals are not antisymmetric; for example, the element with upper indices α,i,β,i is not necessarily zero. One possibility is to apply the purification to the entire 2-RDM. While this procedure ensures that the whole 2-RDM contracts correctly to the 1-RDM, it does not generally produce a 2-RDM whose individual spin blocks contract correctly. Usually the overall 1-RDM is correct only because the α/α -spin block has a contraction error, which cancels with the contraction error from the α/β -spin block.

A better strategy is to introduce a modified unitary decomposition for the α/β block. An appropriate decomposition is

$${}^2D_0^{\alpha,\beta} = \frac{\text{Tr}({}^2D^{\alpha,\beta})}{r_s} {}^1I_\alpha^\alpha {}^1I_\beta^\beta, \quad (41)$$

$${}^2D_1^{\alpha,\beta} = \frac{1}{r_s} \left[{}^1D_\alpha^\alpha - \frac{\text{Tr}({}^1D_\alpha^\alpha)}{r_s} {}^1I_\alpha^\alpha \right] {}^1I_\beta^\beta + \frac{1}{r_s} {}^1I_\alpha^\alpha \left[{}^1D_\beta^\beta - \frac{\text{Tr}({}^1D_\beta^\beta)}{r_s} {}^1I_\beta^\beta \right], \quad (42)$$

and

$${}^2D_2^{\alpha,\beta} = {}^2D^{\alpha,\beta} - {}^2D_1^{\alpha,\beta} - {}^2D_0^{\alpha,\beta}, \quad (43)$$

where r_s denotes the number of spatial orbitals, which equals half the number r of spin orbitals. Like the unitary decomposition for antisymmetric matrices in Sec. II B, the zeroth component ${}^2D_0^{\alpha,\beta}$ contains the trace information

$$L_2^0({}^2D_0^{\alpha,\beta}) = \text{Tr}({}^2D_0^{\alpha,\beta}) = \text{Tr}({}^2D^{\alpha,\beta}), \quad (44)$$

and the first component ${}^2D_1^{\alpha,\beta}$ contains the one-particle information except for the trace

$$L_2^1({}^2D_0^{\alpha,\beta} + {}^2D_1^{\alpha,\beta}) = \frac{N}{2} {}^1D_\alpha^\alpha. \quad (45)$$

The two-particle component of ${}^2D^{\alpha,\beta}$ carries information that vanishes upon contraction,

$$L_2^1({}^2D_2^{\alpha,\beta}) = 0, \quad (46)$$

where the 0 represents the zero matrix. The purification process for the 2-RDM's α/β block remains the same as described in Sec. II D except that the decomposition in Eqs. (41)–(43) is employed.

III. APPLICATIONS

The purification of correlated RDMs may be illustrated through the solution of the CSE by the contracted power method. In each iteration of the N -particle power method, a new trial wave function is produced through the application of the Hamiltonian to the current trial wave function [51]. Analogously, in each iteration of the contracted power method we generate a new trial 2-RDM by applying the Hamiltonian to the current 2-RDM through the CSE with reconstruction [7,20]. We employ the second-order correction for the 3-RDM in Refs. [12,15]. After each iteration of the CSE we apply the purification algorithm to improve the positivity of the two-particle and the two-hole RDMs. Known as the D and the Q conditions, respectively, these positivity constraints are necessary for a 2-RDM to correspond to an N -particle density matrix. Additional details concerning the contracted power method for solving the CSE will be presented elsewhere [20]. Here we focus on (i) demonstrating the 2-RDM purification algorithm and (ii) illustrating its role in stabilizing the convergence of the contracted power iterations (or CSE iterations).

With the contracted power method for the CSE, the water molecule is treated in its equilibrium geometry [52] where the integrals for a split-valence double-zeta basis set [53] are computed with PC GAMESS [54], an implementation of the quantum chemistry package GAMESS (USA) [55]. From the final iteration of the CSE Fig. 1(a) reports the D - and the Q -positivity errors in the α/α block of the 2-RDM as functions of the purification iterations; Fig. 1(b) gives these errors for the α/β block. The D -positivity error in a spin block is the magnitude of the block's most negative eigenvalue *after* the block has been mapped to the two-hole RDM by Eq. (27). With just eight iterations, the purification decreases the errors in the D and the Q conditions for the α/α block by an order of magnitude to less than 10^{-5} , and with 20 iterations the errors in the D and the Q conditions for the α/β block are decreased by almost two orders of magnitude.

The purification algorithm also improves the positivity for each molecule given in Tables I and II. All molecules are computed with equilibrium geometries [52] in a split-valence double-zeta basis set [53] except for N_2 and CO, which are treated with Slater-type orbitals expanded in six Gaussians [54,55]. From the final CSE iteration for each molecule, Tables I and II give the positivity errors in the D and the Q conditions *before* and *after* purification. The purification algorithm consistently decreases the error in the D and the Q conditions by more than one order of magnitude. Purification of the α/α block generally requires fewer iterations than the purification of the α/β block. Further details of these calculations and the contracted power method that are not specific to purification will be presented elsewhere [20].

The data presented demonstrates the effectiveness of the purification algorithm as a general tool for imposing N -representability conditions iteratively upon the 2-RDM. More specifically, we now examine the effect of purification on solving the CSE by the contracted power method. For the H_2O molecule Figs. 2(a) and 2(b) report the D - and the Q -positivity errors in the α/β block as functions of the CSE

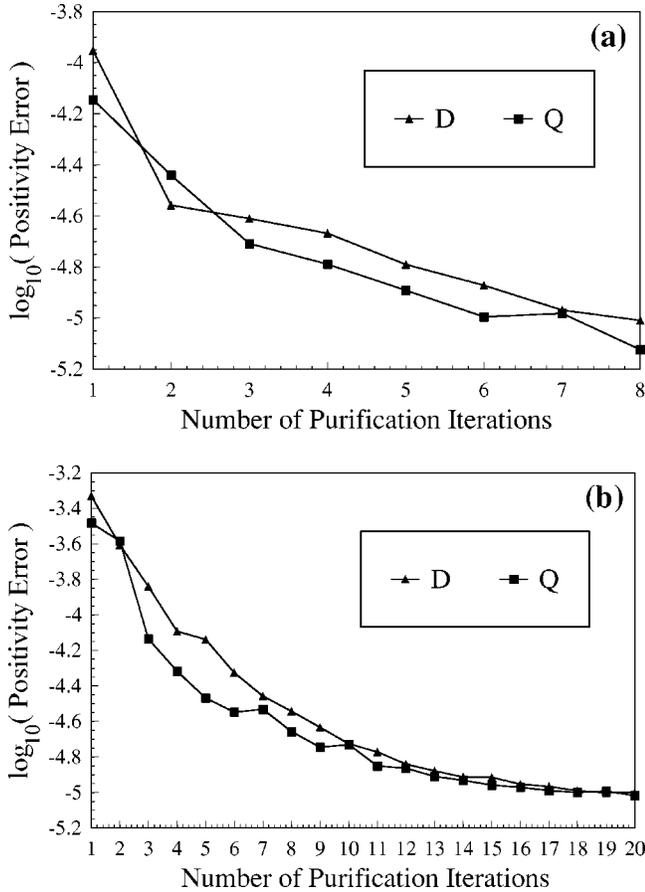


FIG. 1. From the final iteration of the CSE (a) the D - and the Q -positivity errors in the α/α block of the 2-RDM are reported as functions of the purification iterations, (b) the D - and the Q -positivity errors in the α/β block are given.

iterations. Both the D - and the Q -positivity errors reveal that purification increases significantly with the number of CSE iterations. By the final iteration the two-particle and the two-hole RDMs are purified by nearly two orders of magnitude. Figure 3 shows the ground-state electronic energy for H_2O as a function of the CSE iterations both *with* and *without* purification. While the CSE with purification captures 92.8% of

the correlation energy, the CSE *without* purification obtains only 71.2% of the correlation energy before diverging. Although the unpurified energy increases after its minimum in the case of water, the energy without purification has also been observed to decrease significantly below the full-configuration-interaction energy. The contracted power method with purification, overcoming the convergence problems reported by Yasuda and Nakatsuji [6,10,19], displays consistent and reliable movement towards the N -particle solution at each CSE iteration.

IV. CONCLUSIONS

Purification, both as a concept and an algorithm, has been developed for correlated reduced density matrices. The term purification typically refers to the process of making a 1-RDM idempotent. This kind of purification, originating in McWeeny's work [21], is significant in the modern linear-scaling literature [22–24] where it enforces 1-RDM N representability. Every idempotent 1-RDM is N representable with a unique preimage, which is an N -particle Slater determinant. We define *purification of correlated RDMs* to be the iterative process by which an arbitrary p -particle density matrix is projected onto a p -RDM, which obeys significant necessary conditions for N representability. In this paper we developed a purification algorithm for the 2-RDM although the ideas presented are readily extended to the purification of higher RDMs.

The purification procedure for the 2-RDM first checks whether it contracts to an N -representable 1-RDM. If the 1-RDM requires adjustment, the 2-RDM is updated through the unitary decomposition, which reveals the portion of the 2-RDM that contributes to the 1-RDM via contraction. When combined with the cumulant formula for the 2-RDM, the unitary decomposition determines all of the 2-RDM except the two-particle unitary portion of the connected 2-RDM. The remaining 2-RDM portion may be further purified through the satisfaction of 2-RDM positivity conditions. We employ the D condition and the Q condition (from particle-hole duality) on the 2-RDM although additional conditions, such as the G condition, may also be incorporated [17]. The trial 2-RDM and its two-hole RDM have negative eigenval-

TABLE I. Purification of two-particle and two-hole RDMs α/α block

Molecule	Number of purification iterations	Lowest eigenvalue			
		${}^2D_{\alpha,\alpha}^{\alpha,\alpha}$		${}^2\bar{D}_{\alpha,\alpha}^{\alpha,\alpha}$	
		Initial	Final	Initial	Final
BeH_2	15	-8.81×10^{-5}	-8.55×10^{-6}	-4.19×10^{-4}	-9.09×10^{-6}
BH	13	-1.74×10^{-4}	-9.45×10^{-6}	-4.30×10^{-4}	-6.74×10^{-6}
CH_4	18	-3.95×10^{-4}	-9.65×10^{-6}	-2.83×10^{-4}	-8.91×10^{-6}
CO	5	5.71×10^{-5}	-1.29×10^{-12}	-1.18×10^{-4}	-6.87×10^{-6}
H_2O	19	-2.18×10^{-4}	-1.21×10^{-5}	-1.82×10^{-4}	-7.65×10^{-6}
HF	7	-9.93×10^{-5}	-8.62×10^{-6}	-7.13×10^{-5}	-7.50×10^{-6}
N_2	5	8.33×10^{-5}	-4.16×10^{-12}	-1.43×10^{-4}	-6.78×10^{-6}
NH_3	13	-2.92×10^{-4}	-9.27×10^{-6}	-3.25×10^{-4}	-7.65×10^{-6}

TABLE II. Purification of two-particle and two-hole RDMs α/β block

Molecule	Number of purification iterations	Lowest eigenvalue			
		${}^2D_{\alpha,\beta}^{\alpha,\beta}$		${}^2\bar{D}_{\alpha,\beta}^{\alpha,\beta}$	
		Initial	Final	Initial	Final
BeH ₂	20	-5.21×10^{-4}	-4.86×10^{-5}	-4.95×10^{-4}	-2.92×10^{-5}
BH	14	-7.04×10^{-4}	-8.51×10^{-5}	-5.95×10^{-4}	-7.10×10^{-5}
CH ₄	20	-1.19×10^{-3}	-1.35×10^{-5}	-5.77×10^{-4}	-1.24×10^{-5}
CO	8	1.35×10^{-4}	-1.03×10^{-13}	-1.16×10^{-4}	-9.75×10^{-6}
H ₂ O	17	-1.08×10^{-3}	-2.44×10^{-5}	-9.82×10^{-4}	-1.76×10^{-5}
HF	18	-6.99×10^{-4}	-9.69×10^{-6}	-5.77×10^{-4}	-9.48×10^{-6}
N ₂	20	1.77×10^{-4}	-2.50×10^{-13}	-1.07×10^{-4}	-9.90×10^{-6}
NH ₃	20	-1.06×10^{-3}	-1.16×10^{-5}	-9.26×10^{-4}	-1.03×10^{-5}

ues whose eigenvectors correspond to the two-particle matrices that expose the 2-RDM. Through the unitary decomposition a procedure is developed whereby the 2-RDM is adjusted, without modifying its contraction to the 1-RDM, to prevent it from being exposed by a certain set of operators. Repeating this process systematically purifies the 2-RDM.

The contracted power method employs purification in solving the 2,4-CSE for the 2-RDM. Purification of correlated 2-RDMs works with the reconstruction of the 3- and

the 4-RDMs to enable the solution of the 2,4-CSE for N -particle information. While other schemes for solving the 2,4-CSE by self-consistent iteration have exhibited convergence problems [6,10,19], the contracted power method with purification moves systematically and reliably towards N -particle energies and 2-RDMs. The change in the 2-RDM in the contracted power method is essentially a “gradient,” which minimizes the N -particle energy [20]. The purification does not interfere with this “gradient” but rather improves it through the removal of the portion that does not preserve N representability. The good CSE convergence for BeH₂ obtained by Valdemoro, Tel, and Perez-Romero is most likely due to an implicit purification of the 2-RDM present in their RDM “renormalization” methods, which fix the trace and the positivity of the diagonal elements [4,14,19]. Applying the contracted power method for the molecule H₂O *without* purification produces a premature minimum in the energy, which is followed by divergence while the same calculation with purification yields an accurate, stable solution of the CSE. Further results and details of the contracted power method will be presented elsewhere [20].

More than a useful tool in solving the CSE, purification

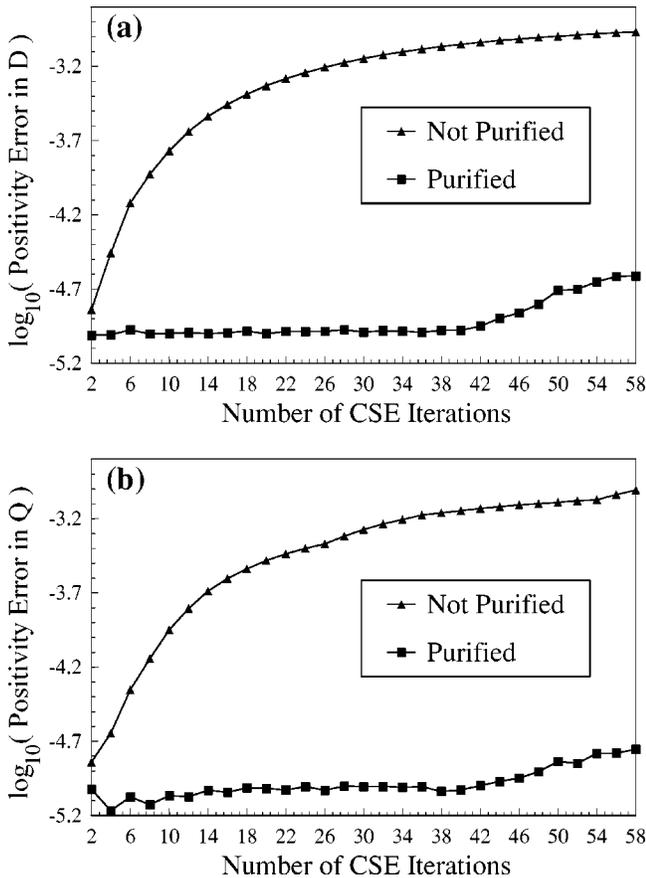


FIG. 2. The D - and the Q -positivity errors in the α/β block are reported in (a) and (b), respectively, as functions of the CSE iterations.

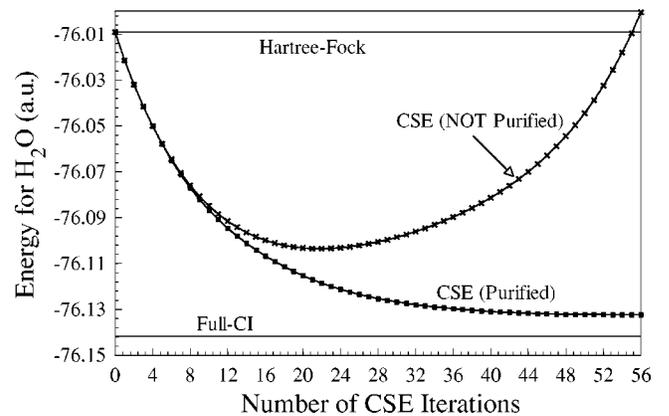


FIG. 3. The ground-state electronic energy for H₂O is shown as a function of the CSE iterations both *with* and *without* purification. The CSE with purification captures 92.8% of the correlation energy, but the CSE *without* purification achieves only 71.2% of the correlation energy before diverging.

offers a general approach for imposing N -representability conditions on reduced density matrices. Traditional work on energy optimization with the 2-RDM employs the N -representability conditions as constraints on the minimization [30–32]. While new techniques for positive semidefinite programming have been recently developed by the applied mathematics community [56,57], constrained optimization of the N -particle energy is still computationally challenging [17,33]. Linear-scaling algorithms for Hartree-Fock and density-functional theories were realized when purification permitted the incorporation of 1-RDM N -representability conditions into an unconstrained energy minimization [22–24]. Similarly, purification of correlated 2-RDMs provides an iterative, unconstrained approach to the enforcement of N -representability conditions, which promises further advances in reduced density-matrix methods for correlated many-body systems.

ACKNOWLEDGMENTS

The author expresses his appreciation to Professor Herschel A. Rabitz, Professor Dudley R. Herschbach, and Dr. Alexander R. Mazziotti for their support and encouragement. The NSF is gratefully acknowledged for support.

APPENDIX: WEDGING AND CONTRACTING

An important tool in many-body theory is the antisymmetrized tensor product, known as the wedge (or Grassmann) product [7,18,58], which is denoted by the symbol \wedge . Consider the wedge product between two matrices 1A and 1B ,

$${}^2C = {}^1A \wedge {}^1B. \quad (\text{A1})$$

The elements $c_{k,l}^{i,j}$ of 2C may be computed from a_k^i and b_l^j by summing the distinct products arising from all antisymmetric permutations of the upper and the lower indices. For the wedge product of one-particle matrices there are only four distinct possibilities,

$${}^2c_{k,l}^{i,j} = \frac{1}{4}(a_k^i b_l^j - a_l^i b_k^j - a_k^j b_l^i + a_l^j b_k^i). \quad (\text{A2})$$

In general, the elements of the wedge product may be expressed as

$$a_{j_1, j_2, \dots, j_p}^{i_1, i_2, \dots, i_p} \wedge b_{j_{p+1}, \dots, j_N}^{i_{p+1}, \dots, i_N} = \left(\frac{1}{N!} \right)^2 \sum_{\pi, \sigma} \epsilon(\pi) \epsilon(\sigma) \pi \sigma a_{j_1, j_2, \dots, j_p}^{i_1, i_2, \dots, i_p} b_{j_{p+1}, \dots, j_N}^{i_{p+1}, \dots, i_N}, \quad (\text{A3})$$

where π represents all permutations of the upper indices and σ represents all permutations of the lower indices while the function $\epsilon(\pi)$ returns +1 for an even number of transpositions and -1 for an odd number of transpositions. The total number of permutations is $(N!)$ ²; hence, the division by this factor for normalization. If elements of the matrices pA and ${}^{N-p}B$ are assumed antisymmetric, then the total number of distinct permutations is $[N!/(p!(N-p)!)]^2$, which we would employ for the normalization. Other symmetries may also be incorporated into the definition with an appropriate change in the normalization (i.e., when ${}^pA = {}^{N-p}B$).

A tool complementary to the wedge product in many-body theory is the contraction operator, which we denote by L . Consider the contraction of a N -particle matrix ${}^N A$ to a p -particle matrix ${}^p B$,

$${}^p B = L_N^p({}^N A). \quad (\text{A4})$$

The contraction operator generates the elements of ${}^p B$ from the elements of ${}^N A$ by the prescription

$$b_{j_1, j_2, \dots, j_p}^{i_1, i_2, \dots, i_p} = \sum_{i_{p+1}, \dots, i_N} a_{j_1, \dots, j_p, i_{p+1}, \dots, i_N}^{i_1, \dots, i_p, i_{p+1}, \dots, i_N}. \quad (\text{A5})$$

The operator L provides a convenient notation for discussing the contraction mapping without a plethora of indices.

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