Necessary conditions for the *N*-representability of the second-order reduced density matrix: Upper bounds on the *P* and *Q* matrices

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Usually, variational calculations for the second-order reduced density matrix are performed subject to the constraint that the "*P*" and "*Q*" matrices are positive semidefinite, which only constrains the lowest eigenvalue of these matrices. We characterize the highest eigenvalue of these matrices and discuss how the associated constraint (which is related to the ground-state energy of the Hamiltonians $H=-P$ and $H=-Q$) can be implemented in practical calculations. This necessary condition for *N*-representability should help ensure that the second-order reduced density matrix is not "overcorrelated."

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I. BACKGROUND

Recently, there has been a rekindling of interest in approaches to the electronic structure problem based on variational optimization of the second-order reduced density matrix [1–9], which is variously expressed as a position-dependent integral kernel,

$$\Gamma_2(z_1,z_2;z_1',z_2') \equiv \sum_i w_i \left[\frac{1}{4} \sum_{j,k,j',k'} \{(\psi_j(z_1)\psi_k(z_2) - \psi_j(z_2)\psi_k(z_1))\langle\Psi_i|a_j^\dagger a_{k'}^\dagger a_k a_j|\Psi_i\rangle \times(\psi_{k'}(z_2')\psi_{j'}(z_1') - \psi_{k'}(z_1')\psi_{j'}(z_2'))\} \right], \tag{1}$$

as a matrix,

$$\Gamma_{2;jk;j'k'} = \sum_i w_i \langle\Psi_i|a_j^\dagger a_{k'}^\dagger a_k a_j|\Psi_i\rangle, \tag{2}$$

or as an operator on a two-electron Hilbert space,

$$\hat{\Gamma}_2 = \sum_i w_i \left[\frac{1}{4} \sum_{j,k,j',k'} \{|\psi_j\psi_k\rangle\langle\Psi_i|a_j^\dagger a_{k'}^\dagger a_k a_j|\Psi_i\rangle\langle\psi_{j'}\psi_{k'}|\} \right]. \tag{3}$$

Here, $z_i=(\boldsymbol{r}_i,\sigma_i)$ denotes both the space and the spin of electron i, a_j and $a_j^\dagger$ are the operators for annihilating and creating the spin orbital $\psi_j(z)$, and $|\psi_j\psi_k\rangle$ is a normalized two-electron Slater determinant. We adopt the usual conventions of quantum chemistry and restrict ourselves to real orbitals. The weights, w_i, are nonnegative and must sum to unity, so that $\hat{\Gamma}_N=\Sigma_i w_i|\Psi_i\rangle\langle\Psi_i|$ represents an ensemble average of *N*-electron systems.

Any second-order reduced density that can be written in the form of Eqs. (1)–(3) is said to be *N*-representable [10–13]. It then follows from the fundamental variational principle for the energy,

$$E_{g.s.}[\hat{H}_N] = \min_{\Gamma_N} \mathrm{Tr}[\hat{H}_N\hat{\Gamma}_N], \tag{4}$$

that the ground-state energy can be rewritten as a variational procedure with respect to Γ_2 whenever the *N*-body Hamiltonian contains at most two-body terms. First one introduces the effective (or "reduced") two-electron Hamiltonian operator,

$$\hat{H}_2^{(N)} = \frac{1}{4} \sum_{j,k,j',k'} H_{2;jk,j'k'}^{(N)} a_j^\dagger a_k^\dagger a_{k'} a_{j'}, \tag{5}$$

where

$$H_{2;jk,j'k'}^{(N)} = \langle\psi_j\psi_k| \left\{ \frac{1}{(N-1)} \left(-\frac{\nabla_1^2+\nabla_2^2}{2} + v(\boldsymbol{r}_1) + v(\boldsymbol{r}_2) \right) + \frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \right\} |\psi_{j'}\psi_{k'}\rangle. \tag{6}$$

Then one minimizes the energy with respect to the constraint that Γ_2 must be *N*-representable, i.e.,

$$E_{g.s.}[\hat{H}_N] = \min_{N\text{–rep}\cdot\Gamma_2} \mathrm{Tr}[\hat{H}_2^{(N)}\hat{\Gamma}_2]. \tag{7}$$

In Eqs. (4) and (7), the "Trace" notation is implemented in the operator representation by adding up all the expectation values of the product operator, $\hat{H}_N\hat{\Gamma}_N$ or $\hat{H}_2^{(N)}\hat{\Gamma}_2$, in any appropriate complete basis. Equivalently, one can regard the density matrices and Hamiltonian operators as matrices, with the antisymmetry of the two-electron states reflected in the matrix trace,

$$\mathrm{Tr}[H_2^{(N)}\Gamma_2] = \sum_{j<k;j'<k'} H_{2;jk,j'k'}^{(N)} \Gamma_{2;j'k',jk} = \frac{1}{4} \sum_{j,k;j',k'} H_{2;jk,j'k'}^{(N)} \Gamma_{2;j'k',jk}. \tag{8}$$

In the coordinate-space representation [Eq. (1)], the equivalent operation is: apply the Hamiltonian operator, set all the primed and unprimed variables equal, and integrate over the remaining coordinates. For simplicity, in what follows, we

will adopt the orbital-based, rather than the coordinate-space, representations.

Were it not for the N-representability constraint in Eq. (7), the N-electron problem would be comparable in difficulty to the two-electron problem. The exact N-representability conditions are known [12]. $\hat{\Gamma}_2$ is N-representable if and only if, for every N-body Hamiltonian, $\hat{H}_N$,

$$E_{g.s.}[\hat{H}_N] \leqslant \mathrm{Tr}[\hat{H}_2^{(N)}\hat{\Gamma}_2]. \tag{9}$$

Clearly if Eq. (9) does not hold, then $\hat{\Gamma}_2$ violates the variational principle, and so cannot be N-representable. The converse is also true, and merely indicates that if $\hat{\Gamma}_2$ is not N-representable, then there will exist at least one Hamiltonian that is capable of "diagnosing" this malady. This is ordinarily proved with the polar cone theorem [12], but a three-line proof of the result is included as the Appendix.

Because it is impractical to ensure that Eq. (9) holds for *all* Hamiltonians, one typically requires this only for a subset of Hamiltonians. The three most common constraints are embodied by the P, Q, and G conditions [10,12], which are based on the positive semidefiniteness of

$$\hat{H}_N = \hat{B}^\dagger \hat{B} \geqslant 0, \tag{10}$$

where $\hat{B}^\dagger$ denotes the conjugate transpose of $\hat{B}$. Specifically, for the P condition, one chooses

$$\hat{B}(\{p_{jk}\}) = \sum_{j,k=1}^{K} p_{jk} a_k a_j, \tag{11}$$

with $p_{jk}=-p_{kj}$. For the Q condition, one chooses

$$\hat{B}(\{q_{jk}\}) = \sum_{j,k=1}^{K} q_{jk} a_k^\dagger a_j^\dagger, \tag{12}$$

with $q_{jk}=-q_{kj}$. For the G condition, one chooses

$$\hat{B}(\{g_{jk}\}) = \sum_{j,k=1}^{K} g_{jk} a_k^\dagger a_j. \tag{13}$$

In Eqs. (11)–(13), K is the number of spin orbitals in the basis set. We assume that K is even, which is true whenever all of the α-spin and β-spin orbitals associated with a given spatial basis are included. For convenience, we will also assume that the one-electron basis set is large enough to be interesting, so that the electron number is below half-filling (i.e., $N \leqslant K/2$). "Proof-of-principle" density-matrix calculations typically use small basis sets where this is not true. To apply our results to these cases, particle-hole symmetry is used to convert the N-electron problem to an $(M=K-N)$-hole problem. The number of holes is now below half-filling, so all of our results still hold, except that the P condition for the electrons becomes the Q condition for the holes, and vice versa.

Hamiltonians with the form of Eq. (10) are not very realistic models for atoms and molecules. In atoms and molecules, the ground-state energy is negative and, if the ground state is degenerate, the degree of degeneracy is typically small. By contrast, the ground state of the Hamiltonians associated with the P condition is usually highly degenerate and has a ground-state energy of zero. This is most easily seen by transforming the single-particle basis so that $\hat{B}$ has its canonical "pairing" form [14–16], with the transformed orbitals linked together in a pairwise manner. If we order the orbitals so that each odd orbital is paired with the even orbital directly after it, then Eq. (11) can be rewritten as

$$\hat{B}(p_j) = \sum_{j=1}^{K/2} p_j a_{2j-1} a_{2j}, \tag{14}$$

where the pairing strength parameters, p_j, are real. Clearly $\hat{B}^\dagger \hat{B}|\Phi\rangle = 0$ whenever Φ is a Slater determinant that includes orbitals but not their pairs. For example, $\hat{B}^\dagger \hat{B}|\phi_2 \phi_4 \cdots \phi_{2N}\rangle = 0$ because all the orbitals that are paired with the orbitals in this Slater determinant are missing.

The Hamiltonian $-\hat{B}^\dagger \hat{B}$ seems more realistic. The ground-state energy would now be negative, and typically nondegenerate. We expect, then, that bounds of the form,

$$E_{g.s.}[-\hat{B}^\dagger \hat{B}] \leqslant \mathrm{Tr}[-\hat{B}^\dagger \hat{B}\Gamma_2] \tag{15}$$

would provide meaningful N-representability constraints. These constraints can be compactly rewritten as upper bounds on the eigenvalues of the P, Q, and G matrices; this gives the constraint that

$$0 \leqslant \mathrm{Tr}[\hat{B}^\dagger \hat{B}\Gamma_2] \leqslant -E_{g.s.}[-\hat{B}^\dagger \hat{B}] \tag{16}$$

for all N-representable Γ_2.

The aim of the present paper is to derive N-representability constraints of precisely this form. We are fortunate in that, for the forms of $\hat{B}$ associated with the P and Q conditions, we can find the eigenvalues of $\hat{B}^\dagger \hat{B}$ analytically. This then provides an "upper bound" to the usual P and Q matrices. In the next two sections of this paper, we will develop improved bounds using exact solutions for the Hamiltonians associated with the P and Q conditions.

II. UPPER BOUNDS TO $\hat{P} \equiv (\Sigma_{j'=1}^{K/2} p_{j'} a_{2j'}^\dagger a_{2j'-1}^\dagger)(\Sigma_{j=1}^{K/2} p_j a_{2j-1} a_{2j})$

In order to provide upper bounds to the matrix associated with the P condition, we again rewrite Eq. (11) in the form of Eq. (14). In addition, it is convenient to set the energy scale for the Hamiltonian so that

$$1 = \sum_{j=1}^{K/2} p_j^2. \tag{17}$$

We are interested in the largest eigenvalue, $\lambda_{\max}(\{p_j\})$ of the Hamiltonian $\hat{P} \equiv \hat{B}(\{p_j\})^\dagger \hat{B}(\{p_j\})$, since this gives a constraint with the form of Eq. (16),

$$0 \leqslant \mathrm{Tr}[\hat{P}(\{p_j\})\Gamma_2] \leqslant \lambda_{\max}(\{p_j\}). \tag{18}$$

$\hat{P}$ belongs to a class of exactly solvable quantum many-body Hamiltonians known as the Richardson-Gaudin [17–19] pairing models. (See Refs. [20–22] for recent reviews.) We state without proof that the relevant eigenvalues of $\hat{P}$ are given by

$$E = 1 - \sum_{\nu=1}^{N/2-1} \frac{2}{y_\nu}, \tag{19}$$

where the $\{y_\nu\}$ are determined by solving a set of $\frac{N}{2}-1$ coupled nonlinear equations,

$$\left\{ \sum_{j=1}^{K/2} \frac{p_j^2}{1 - y_\nu p_j^2} + 2\left(\frac{1}{y_\nu} + \sum_{\mu \neq \nu} \frac{1}{y_\nu - y_\mu} \right) = 0 \right\}_{\nu=1}^{N/2-1}. \tag{20}$$

We refer to Refs. [22–24] for more details on the specific context of Hamiltonians of $\hat{P}$ type and for the lengthy derivation of its eigenvalue spectrum and the corresponding eigenstates. Note that the eigenvalues depend only on the strength parameters, p_j, of the pairing vector in the Hamiltonian [cf. Eq. (14)], and not on the choice of single-particle orbitals.

Equations (19) and (20) hold for an even number of electrons, N (extension to an odd electron number poses no special difficulties) and for the "fully paired" eigenspace of $\hat{P}$. The term fully paired—also called "zero seniority" [25] in this context—indicates that in the wave functions $|\Psi\rangle$ under consideration, no orbital is present without its paired orbital. (Thus, if $|\Psi\rangle$ is expanded in Slater determinants, the orbitals $\psi_{2j-1}(z)$ and $\psi_{2j}(z)$ are simultaneously occupied or unoccupied in each Slater determinant contributing to $|\Psi\rangle$.) Since the fully paired eigenspace contains the extremal eigenvalues that are of interest for the present investigation, Eqs. (19) and (20) are all that is required.

The upper bound in Eq. (18) is distinguished from the usual N-representability constraints because it asserts more than the mere positive semidefiniteness of a matrix. This has advantages (e.g., we have argued that the upper bound is associated with a more realistic Hamiltonian than the lower bound) but also has disadvantages: one must solve a system of nonlinear equations in order to determine $\lambda_{\max}(\{p_j\})$. Efficient methods for solving these equations exist [26], especially when only the largest eigenvalue is needed. However, it is still impractical to solve these equations for the infinite number of possible choices of parameters in the Hamiltonian.

We propose to circumvent this problem in a straightforward manner: at every stage in the density-matrix minimization algorithm, choose the free parameters in the Hamiltonian so that the constraint is as tight as possible. Suppose, for example, that at the ith iteration of the variational procedure, the (approximate) density matrix is $\Gamma_2^{(i)}$. Then we will seek the choice of parameters in the Hamiltonian that maximizes

$$F(\Gamma_2^{(i)};\{p_j\}) = \mathrm{Tr}[\hat{B}^\dagger \hat{B} \hat{\Gamma}_2^{(i)}] - \lambda_{\max}(\{p_j\}). \tag{21}$$

Note that since $\Gamma_2^{(i)}$ is generally *not* N-representable, the maximum value will commonly be positive. This procedure will produce a Hamiltonian, which can be used to constrain the density matrix in the next iteration.

Because $\lambda_{\max}(\{p_j\})$ depends only on the interaction strengths, there is an inherent arbitrariness in the choice of spin orbitals and the pairing between them. This is captured by introducing new creation-annihilation operators, linked to the old ones by a real-orthogonal transformation of the single-particle basis,

$$\mathfrak{a}_k = \sum_{j=1}^{K} U_{kj} a_j. \tag{22}$$

We can then write the Hamiltonian of interest as [cf. Eq. (14)],

$$\begin{aligned} \hat{B}^\dagger \hat{B} &= \sum_{k,k'=1}^{K/2} p_{k'} p_k \mathfrak{a}_{2k'}^\dagger \mathfrak{a}_{2k'-1}^\dagger \mathfrak{a}_{2k-1} \mathfrak{a}_{2k} \\ &= \sum_{k,k'=1}^{K/2} p_{k'} p_k \sum_{j_1,j_2,j_1',j_2'=1}^{K} (U_{2k',j_1'} U_{2k'-1,j_2'} U_{2k,j_1} \\ &\quad \times U_{2k-1,j_2} a_{j_1'}^\dagger a_{j_2'}^\dagger a_{j_2} a_{j_1}). \end{aligned} \tag{23}$$

Referring back to the definition of the density matrix in the second quantization, Eq. (2), we need to determine the choices of p's and U's that maximize

$$\begin{aligned} F(\{p_k\},\{U_{kj}\}) \equiv \sum_{k,k'=1}^{K/2} p_{k'} p_k \sum_{j_1,j_2,j_1',j_2'=1}^{K} (U_{2k',j_1'} U_{2k'-1,j_2'} \\ \times U_{2k,j_1} U_{2k-1,j_2} \Gamma_{2;j_1 j_2 j_1' j_2'}) - \lambda_{\max}(\{p_j\}). \end{aligned} \tag{24}$$

This can be solved by an optimization procedure, with the gradients given by

$$\begin{aligned} \frac{\partial F}{\partial U_{lm}} = \sum_{k,k'=1}^{K/2} p_{k'} p_k \sum_{j_1,j_2,j_1',j_2'=1}^{K} (&\delta_{2k',l} \delta_{j_1',m} U_{2k'-1,j_2'} U_{2k,j_1} U_{2k-1,j_2} \\ &+ U_{2k',j_1'} \delta_{2k'-1,l} \delta_{j_2',m} U_{2k,j_1} U_{2k-1,j_2} \\ &+ U_{2k',j_1'} U_{2k'-1,j_2'} \delta_{2k,l} \delta_{j_1,m} U_{2k-1,j_2} \\ &+ U_{2k',j_1'} U_{2k'-1,j_2'} U_{2k,j_1} \delta_{2k-1,l} \delta_{j_2,m}) \Gamma_{2;j_1 j_2 j_1' j_2'}, \end{aligned} \tag{25}$$

or, equivalently,

$$\begin{aligned} \frac{\partial F}{\partial U_{2k-\eta,m}} = \sum_{k'=1}^{K/2} \sum_{n_1 n_2 n_3 = 1}^{K} (2 p_k p_{k'} U_{2k'-1+\eta,n_1} \\ \times U_{2k'-\eta,n_2} U_{2k-1+\eta,n_3} \Gamma_{2;n_1 n_2 n_3 m}), \end{aligned} \tag{26}$$

with $k = 1,2,\ldots,K/2$ and $\eta = 0,1$.

The derivatives with respect to the pairing strengths are given by

$$\begin{aligned} \frac{\partial F}{\partial p_r} = 2 \sum_{k=1}^{K/2} p_k \sum_{j_1,j_2,j_1',j_2'=1}^{K} U_{2r,j_1'} U_{2r-1,j_2'} U_{2k,j_1} U_{2k-1,j_2} \Gamma_{2;j_1 j_2 j_1' j_2'} \\ - \frac{\partial \lambda_{\max}(\{p_j\})}{\partial p_r}, \end{aligned} \tag{27}$$

where

$$\frac{\partial \lambda_{\max}}{\partial p_r} = 2 \sum_{\nu=1}^{N/2-1} \left(\frac{\partial y_\nu}{\partial p_r} \right) \frac{1}{(y_\nu)^2}. \tag{28}$$

and the derivatives, $\frac{\partial y_\nu}{\partial p_k}$, are obtained by solving the linear equations,

$$\left\{ 0 = \frac{\partial y_\nu}{\partial p_k} \left[\sum_{j=1}^{K/2} \frac{p_j^4}{(1-y_\nu p_j^2)^2} - \frac{2}{y_\nu^2} - \sum_{\mu \neq \nu} \left(\frac{2}{(y_\nu - y_\mu)^2} \right) \right] + \sum_{\mu \neq \nu} \frac{\partial y_\mu}{\partial p_k} \left(\frac{2}{(y_\nu - y_\mu)^2} \right) + \frac{2p_k}{(1-y_\nu p_k^2)^2} \right\}_{\nu=1}^{N/2-1}. \tag{29}$$

The normalization constraint, Eq. (17), and the orthogonality conditions on the orbital transformations,

$$\sum_k U_{kj} U_{kl} = \delta_{jl} \tag{30}$$

are readily enforced using Lagrange multipliers. Note that the nonlinear equations must be solved at each iteration of the procedure, as the solutions of the nonlinear equations are required to determine $\frac{\partial y_\nu}{\partial p_k}$.

III. BOUNDS TO $\hat{Q} \equiv (\Sigma_{j'=1}^{K/2} q_{j'} a_{2j'} a_{2j'-1})(\Sigma_{j=1}^{K/2} q_j a_{2j-1}^\dagger a_{2j}^\dagger)$

When we choose $\hat{B}$ to have the appropriate form for the Q condition, Eq. (12), relevant bounds for the Hamiltonian, $\hat{H}_N = \hat{B}^\dagger \hat{B}$ can be found using methods similar to those in the previous section. Just as before, the first step is to transform to the one-electron basis set so that $\hat{B}$ is expressed in terms of orbital pairs,

$$\hat{B}(\{q_j\}) = \sum_{j=1}^{K/2} q_j a_{2j-1}^\dagger a_{2j}^\dagger, \tag{31}$$

with real pairing strengths, q_j, and the energy scale chosen so that

$$1 = \sum_{j=1}^{K/2} q_j^2. \tag{32}$$

From this stage, we can solve the Schrödinger equation for $\hat{H}_N = \hat{Q}$, again reducing the problem to a set of nonlinear equations.

Determining the largest eigenvalue is particularly simple. First, note that if λ is a nonzero eigenvalue in the eigenvalue equation $\hat{B}^\dagger \hat{B} |\Psi_N\rangle = \lambda |\Psi_N\rangle$ for $\hat{Q} = \hat{B}^\dagger \hat{B}$, then $\hat{B}|\Psi_N\rangle$ is not zero and it is an eigenvector of the equation,

$$\hat{B}\hat{B}^\dagger \hat{B} |\Psi_N\rangle = \lambda \hat{B} |\Psi_N\rangle. \tag{33}$$

However, we can view this as a Schrödinger equation in the $N+2$-electron space, where the Hamiltonian is $\hat{P} = \hat{B}\hat{B}^\dagger$. Conversely, if λ is a nonzero eigenvalue of the $N+2$-electron eigenproblem, $\hat{B}\hat{B}^\dagger |\Psi_{N+2}\rangle = \lambda |\Psi_{N+2}\rangle$, then $\hat{B}^\dagger |\Psi_{N+2}\rangle \neq 0$ is an N-electron eigenvector of $\hat{Q} = \hat{B}^\dagger \hat{B}$ since

$$\hat{B}^\dagger \hat{B} (\hat{B}^\dagger |\Psi_{N+2}\rangle) = \lambda (\hat{B}^\dagger |\Psi_{N+2}\rangle). \tag{34}$$

We conclude that the N-electron Hamiltonian $\hat{Q}$ and the $N+2$-electron Hamiltonian $\hat{P}$ have the same set of nonzero eigenvalues.

It follows that $\lambda_{\max}(\{q_j\})$, the largest N-electron eigenvalue of $\hat{Q} = \Sigma_{j,k=1}^{K/2} q_j q_k a_{2k} a_{2k-1} a_{2j-1}^\dagger a_{2j}^\dagger$ coincides with the largest $N+2$-electron eigenvalues of $\hat{P} = \Sigma_{j,k=1}^{K/2} q_j q_k a_{2j-1}^\dagger a_{2j}^\dagger a_{2k} a_{2k-1}$. However, since $\hat{P}$ is a Hamiltonian with the same form, we considered in Sec. II, its largest eigenvalue can be determined using the generalization of Eqs. (19) and (20) to $N+2$ electrons. In addition, the same methods can be used to find the choice of pairing strengths, $\{q_j\}$, and the orbital transformation that makes the upper bound in Eq. (16) as effective as possible.

When $\hat{B}$ has the appropriate form for the P condition, Eq. (11), the lowest eigenvalue of $\hat{P} = \hat{B}^\dagger \hat{B}$ is zero for any one-electron basis set that is large enough to be interesting. This is not true when we choose the Hamiltonian to have the appropriate form for the Q condition, Eq. (12). In that case, the lowest eigenvalue is zero if and only if $n_q < N$, where n_q is the number of nonzero strength parameters in Eq. (31). This is highly unlikely to occur in practice. Since the lowest eigenvalue of $\hat{Q}$ is usually greater than zero, it gives an additional relevant constraint. Thus, we can say that

$$0 \leqslant \lambda_{\min}(\{q_j\}) \leqslant \mathrm{Tr}[\hat{B}^\dagger \hat{B} \hat{\Gamma}_2] \leqslant \lambda_{\max}(\{q_j\}), \tag{35}$$

where $\lambda_{\min}(\{q_j\})$ and $\lambda_{\max}(\{q_j\})$ are the smallest and largest eigenvalues of the Hamiltonian $\hat{Q}[\{q_j\}] = \hat{B}^\dagger \hat{B}$, where $\hat{B}$ is given by Eq. (12). This fact—that, except for trivial cases, the lowest eigenvalue of $\hat{Q}$ is not zero—implies, among other things, that the Q condition as commonly applied is not a tight constraint, since it only requires that $\hat{Q}$ be positive semidefinite.

In principle, the lower-bound condition associated with a nonzero $\lambda_{\min}(\{q_j\})$ can be implemented in the same way as the upper bound by using the lowest nonzero solution of Eqs. (19) and (20) for $N+2$ electrons. However, the lower-bound constraint may be less important than the upper-bound constraint, since it is restricted to the interval $0 \leqslant \lambda_{\min}(\{q_j\}) \leqslant 1$. As a consequence, $\lambda_{\min}(\{q_j\})/N$ approaches zero as the number of electrons increases, in contrast to $\lambda_{\max}(\{q_j\})$, which can scale with N. In the following, we therefore assume that only the usual Q condition of positive semidefiniteness is imposed.

IV. PROPOSED ALGORITHM

The results of this procedure should not be hard to implement in any existing density-matrix optimization program [1,3,5,6,9]. At each iteration, i, in the density-matrix optimization procedure, one performs the following steps (in addition to the usual steps in one's optimization procedure):

1. Using the current approximation with the density matrix, $\Gamma_2^{(i)}$, find the choice of coefficients, $\{p_j^{(i)}\}$ and $\{q_j^{(i)}\}$, and

real-orthogonal transformations, $U_{jk}^{(P,i)}$ and $U_{jk}^{(Q,i)}$, that cause the upper bounds on the P and Q conditions to be as tight as possible. The orbital transformations can be obtained using the gradient-based maximization procedure sketched at the end of Sec. II. Specifically, one maximizes $F(\{p_k\},\{U_{jk}^{(-,i)}\})$ [cf. Eq. (24)] using the gradients given in Eqs. (26)–(29).

2. After determining the optimal form of the P and Q Hamiltonians, one has the new constraints, which can be compactly specified using the objective function for the maximization in step 1. For every N-representable density matrix, it must be true that

$$F(\{p_j^{(i)}\},\{U_{jk}^{(P,i)}\}) \leqslant 0,$$

$$F(\{q_j^{(i)}\},\{U_{jk}^{(Q,i)}\}) \leqslant 0. \tag{36}$$

These are simple linear inequality constraints on the density matrix.

3. The linear constraints (36) are imposed when the next step in the density-matrix optimization algorithm is performed. In practice, it might be more useful to impose not only the constraints from the present iteration, but also the constraints associated with a few of the previous iterates. That is, one might impose the series of linear constraints:

$$\left.\begin{matrix} F(\{p_j^{(h)}\},\{U_{jk}^{(P,h)}\}) \leqslant 0 \\ F(\{q_j^{(h)}\},\{U_{jk}^{(Q,h)}\}) \leqslant 0 \end{matrix}\right\}_{h=i-n_i+1}^{i} \tag{37}$$

based on the constraints from the previous n_i iterates.

This algorithm would seem to be particularly amenable to using Mazziotti's first-order nonlinear algorithm [5,6], since these simple linear constraints of this form are readily cast in augmented Lagrangian form using slack variables [27].

V. DISCUSSION

When one seeks to minimize the energy with respect to the second-order reduced density matrix, Γ_2, one must impose some N-representability constraints. (Otherwise the energies are far below the correct answer.) Most commonly, one merely utilizes the positive semidefiniteness of the $\hat{P}$, $\hat{Q}$, and $\hat{G}$ Hamiltonians. That is, one merely uses the fact that

$$\mathrm{Tr}[\hat{B}^\dagger \hat{B} \hat{\Gamma}_2] \geqslant 0, \tag{38}$$

when $\hat{B}$ has the form given by Eqs. (11)–(13). One discovery from this paper is that the lower bound associated with the Q condition is not tight. This is probably not very important in practice, but it is interesting that most Hamiltonians with the form of the "Q" condition are actually positive definite.

This paper supplements the lower bounds in Eq. (38) with *upper* bounds on the $\hat{P}$ and $\hat{Q}$ Hamiltonians:

$$0 \leqslant \mathrm{Tr}[\hat{P}(\{p_j;U_{jk}^{(P)}\})\hat{\Gamma}_2] \leqslant \lambda_{\max}(\{p_j\}), \tag{39}$$

$$0 \leqslant \mathrm{Tr}[\hat{Q}(\{q_j;U_{jk}^{(Q)}\})\hat{\Gamma}_2] \leqslant \lambda_{\max}(\{q_j\}). \tag{40}$$

The best choices for the parameters in the Hamiltonian can be determined using the procedure sketched in Sec. IV. We do not yet have an upper-bound constraint for the $\hat{G}$ Hamiltonian; that is an interesting topic for future study.

The lower bounds force the reduced density matrices for the particles [Eq. (39)] and the holes [Eq. (40)] to be positive semidefinite. This fundamental requirement reflects the fact that the probability a given orbital is occupied is never negative (P condition). The probability that a given orbital is unoccupied is never negative either (Q condition).

The interpretation of the upper-bound constraints is less straightforward. When the strength parameters in the pair vectors are all chosen equal [i.e., $p_j=\sqrt{\frac{2}{K}}$ in Eq. (14) or $q_j=\sqrt{\frac{2}{K}}$ in Eq. (31)] then these constraints reduce to the well-known constraints on the maximum occupation numbers in the particle and hole reduced density matrices [28], i.e., $\lambda_{\max}(\hat{P})=\lambda_{\max}(\Gamma_2)=\frac{N}{2}\left(1-\frac{N-2}{K}\right)$ and $\lambda_{\max}(\hat{Q})=\frac{N+2}{2}\left(1-\frac{N}{K}\right)$. Coleman has focused extensively on cases where these upper bounds are nearly achieved, arguing that density matrices with eigenvalues that approach these upper bounds are associated with strong long-range electron correlations [11,29]. This establishes, among other things, a link to superconductivity, which is one of the main areas of physics where Hamiltonians with this form are considered.

In the limit of large basis sets, the extremal eigenvalues corresponding to the equal-strength pairing vector become $\lambda_{\min}(\hat{P})=0$; $\lambda_{\max}(\hat{P})=\frac{N}{2}$ and $\lambda_{\min}(\hat{Q})=1$; $\lambda_{\max}(\hat{Q})=\frac{N}{2}+1$. Note that these are identical to the extremal eigenvalues of $\hat{P}=\hat{b}^\dagger\hat{b}$ and $\hat{P}=\hat{b}\hat{b}^\dagger$ in a system of $\frac{N}{2}$ bosons, where $\hat{b}^\dagger$ creates a single boson in an arbitrary single-particle state.

By choosing nonequal strength parameters p_j and q_j in all possible ways, one can generate the most general electron pair state, ranging from equal-strength pairs to the other extreme, a two-electron Slater determinant (where only one of the strength parameters is nonzero). Obviously the upper-bound (as well as the lower-bound) constraints discussed in this paper can then be viewed as constraints on the occupation and nonoccupation of such quasibosons (electron pairs) in an N-electron state. (The electron pairs cannot be perfect bosons because of the Pauli principle.) The upper bounds in Eqs. (39) and (40) reflect this fact, encapsulating the highly nonlinear way in which the structure of the Hamiltonian relates to the strength of electron correlations.

Imposing the upper bounds in Eqs. (39) and (40) helps to ensure that the electrons [Eq. (39)] and holes [Eq. (40)] are not "overcorrelated." It is well known, for example, that the N-electron ground-state energy expression in Eq. (7) can be rewritten as

$$\mathrm{Tr}[\hat{H}_2^{(N)}\hat{\Gamma}_2] = \sum_n \varepsilon_n \,\mathrm{Tr}[\hat{B}_n^\dagger \hat{B}_n \hat{\Gamma}_2], \tag{41}$$

where the ε_n are eigenenergies of the reduced Hamiltonian in the two-electron space and $\hat{B}_n^\dagger$ creates the corresponding normalized two-electron eigenstate. By exceeding the maximal occupation of the $\hat{B}_n$ pairs corresponding to the lowest ε_n, overcorrelated density matrices tend to give energies that are significantly smaller than they should be. Imposing the upper-bound constraints in this paper should reduce the overbinding of electrons and improve the quality of the en-

ergy, and other properties, computed using direct optimization algorithms for the reduced density matrix.

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APPENDIX

Γ_2 is N-representable if and only if,

$$E_{g.s.}[\hat{H}_N] \leqslant \mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2]$$

for every N-electron Hamiltonian. The "only if" part of this statement is a trivial consequence of the variational principle. To prove the "if" part, suppose that $\Gamma_2^{\square}$ is not N-representable. Since the set of N-representable 2-matrices is a closed, convex set, the geometric Hahn-Banach theorem indicates that any density matrix that is not in this set can be separated from it by a hyperplane [30,31]. This implies that there exists a Hamiltonian for which $\mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2] \geqslant k$ for all N-representable Γ_2 but for which $\mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2^{\square}] < k$. Using the variational principle for the density matrix, Eq. (7), we have that for any non-N-representable 2-matrix, $\Gamma_2^{\square}$, there exists a Hamiltonian such that

$$\mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2^{\square}] < k \leqslant E_{g.s.}[\hat{H}_N] \leqslant \mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2]. \qquad (42)$$

That is, every non-N-representable 2-matrix gives too low an energy for some Hamiltonian. Thus Γ_2 is N-representable if $E_{g.s.}[\hat{H}_N] \leqslant \mathrm{Tr}[\hat{H}_2^{(N)}\Gamma_2]$ for every N-electron Hamiltonian.

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