PHYSICAL REVIEW A, VOLUME 63, 042113

Uncertainty relations and reduced density matrices: Mapping many-body quantum mechanics onto four particles

David A. Mazziotti[1,2] and Robert M. Erdahl[3]
[1]*Department of Chemistry, Duke University, Durham, North Carolina 27708*
[2]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544*
[3]*Department of Mathematics and Statistics, Queens University, Kingston, Ontario, Canada K7L 3N6*

(Received 25 October 2000; published 21 March 2001)

For the description of ground-state correlation phenomena an accurate mapping of many-body quantum mechanics onto four particles is developed. The energy for a quantum system with no more than two-particle interactions may be expressed in terms of a two-particle reduced density matrix (2-RDM), but variational optimization of the 2-RDM requires that it corresponds to an *N*-particle wave function. We derive *N*-representability conditions on the 2-RDM that guarantee the validity of the uncertainty relations for all operators with two-particle interactions. One of these conditions is shown to be necessary and sufficient to make the RDM solutions of the dispersion condition equivalent to those from the contracted Schrödinger equation (CSE) [Mazziotti, Phys. Rev. A **57**, 4219 (1998)]. In general, the CSE is a stronger *N*-representability condition than the dispersion condition because the CSE implies the dispersion condition as well as additional *N*-representability constraints from the Hellmann-Feynman theorem. Energy minimization subject to the representability constraints is performed for a boson model with 10, 30, and 75 particles. Even when traditional wave-function methods fail at large perturbations, the present method yields correlation energies within 2%.

DOI: 10.1103/PhysRevA.63.042113 PACS number(s): 03.65.Db, 31.10.+z, 71.10.−w, 24.10.Cn

I. INTRODUCTION

In an after-dinner speech at the 1959 Boulder conference Charles Coulson proposed ''banishing'' the wave function from quantum chemistry in favor of the two-particle reduced density matrix (2-RDM) [1]. While prior work had considered this goal [2,3], Coulson's speech—an epic moment in the history of the 2-RDM—brought scientific publicity to the idea of minimizing the electronic energy as a functional of the 2-RDM. Because the electrons are indistinguishable in the wave function and they interact pairwise in the Hamiltonian, the electronic energy may be written as a linear functional of the 2-RDM [2]. The ground-state energy, however, cannot be determined variationally without applying conditions that ensure that the 2-RDM derives from an *N*-particle wave function [3–6]. In 1963 John Coleman christened Coulson's challenge the *N-representability* problem and announced the solution for the one-particle reduced density matrix (1-RDM) [4]: any 1-RDM, normalized to *N*, corresponds to an ensemble of *N*-particle quantum states if and only if all of its occupation numbers lie between zero and 1.

Recent advancements in density-matrix theory include the solution of the contracted Schrödinger equation (CSE) for an approximate 2-RDM without the *N*-particle wave function [7–24,6]. As its name implies, the CSE is a contraction of the *N*-particle Schrödinger equation onto the space of two particles. If the Hamiltonian contains two-particle interactions, the CSE depends upon the 3- and 4-RDMs in addition to the 2-RDM. Although originally derived in 1976 [25–27], the CSE was not successfully solved beyond Hartree-Fock theory until 1994 in the work of Colmenero and Valdemoro [7–9]. Two approaches exist for solving the CSE: (i) *functional reconstruction* in which the indeterminacy of the CSE is removed by expressing the 3- and 4-RDMs as approximate functionals of the 2-RDM [7–24,6], and (ii) *ensemble representability* in which the indeterminacy of the CSE is removed by applying ensemble *N*-representability conditions on the 4-RDM [13,24]. Most research on the CSE has focused on functional reconstruction. However, Colmenero and Valdemoro's original algorithm for functional reconstruction includes simple adjustments to keep the diagonal elements of the 3- and 4-RDMs positive [9,12], and the most recent work of Valdemoro, Tel, and Perez-Romero [21,22] considers in more detail the use of ensemble representability conditions within the framework of functional reconstruction. In this paper we present a systematic collection of ensemble representability conditions for the 4-RDM and explore their applicability to the original formulation of the *N*-representability problem, that is, the variational minimization of the energy as a linear functional of the 2-RDM. A synthesis of the CSE and direct minimization, the present research extends both the ensemble representability method of Mazziotti for solving the CSE subject to non-negativity of the 4-RDM [13,24] and the generalized *lower-bound* method of Erdahl and Jin [28,29], which variationally optimizes the energy subject to positive semidefinite restrictions on the 3-RDM.

Early research on *N*-representability examined the uncertainty relations for simple operators such as position and momentum and even all operators without interactions between particles [30–35]. In this paper we present *N*-representability conditions on the 2-RDM that include the *uncertainty relations* for *all* operators with pairwise interactions. Because the goal is to determine the correlation energy, the uncertainty relations for correlated operators are especially significant as *N*-representability constraints. We show that the uncertainty relations from operators with pairwise interactions are fully satisfied by forcing a collection of linear functionals of the 4-RDM to be positive semidefinite.

A matrix is *positive semidefinite* if and only if all of its eigenvalues are non-negative.

As a part of the synthesis between the CSE and the variational approach, we examine in Sec. III the connection between the CSE and the dispersion condition [36]. The *dispersion* of an operator $\hat{O}$ is the expectation value of $(\hat{O}-\langle\Psi|\hat{O}|\Psi\rangle)^2$ with respect to the wave function Ψ. The dispersion of an operator vanishes for a given wave function if and only if the wave function is an eigenstate of the operator. The vanishing of the dispersion for an operator's eigenstates is known as the *dispersion condition*. Like the CSE the dispersion condition for an operator with no more than two-particle interactions may be evaluated from only a knowledge of the 4-RDM. Without complete N-representability constraints the dispersion condition, like the CSE, has spurious RDM solutions that do not correspond to wave-function solutions of the Schrödinger equation. By contrast, in the set of pure N-representable density matrices both the CSE and the dispersion condition are necessary and sufficient for a 4-RDM to correspond to a solution of the Schrödinger equation [27,13]. However, recent progress on determining RDMs without the wave function has depended exclusively upon the CSE. Is this just a matter of choice, or is there an important difference between these two equations? We show that the CSE and the dispersion condition are equivalent only when an important 4-RDM positivity condition is satisfied. Otherwise, the CSE is strictly stronger than the dispersion condition because it always implies the dispersion condition as well as significant Hellmann-Feynman perturbations.

Using a system of interacting bosons [37–39], we employ some of the 4-RDM N-representability conditions to minimize the energy as a functional of the 2-RDM (where the 2-RDM is expressed in terms of the 4-RDM by contraction). The present conditions on the 2-RDM yield correlation energies that are several orders of magnitude more accurate than those from traditional techniques like many-body perturbation and coupled-cluster theories. Even for strong interactions where the conventional schemes fail, the current method determines the correlation energy within a few percent. The results are orders of magnitude better than those that can be achieved through functional reconstruction within the CSE [13,23]. In addition to achieving variational minimization without the wave function, we employ the representability conditions to solve the CSE and the dispersion condition.

II. UNCERTAINTY RELATIONS

Let us consider the ground-state wave function $|\Psi\rangle$ of an N-particle Hamiltonian with no more than pairwise interactions. Using an orbital basis set in the notation of second quantization, we have

$$\hat{H}=\sum_{m,n,p,q} {}^2K^{m,n}_{p,q}\hat{a}^{\dagger}_m\hat{a}^{\dagger}_n\hat{a}_q\hat{a}_p , \qquad (1)$$

where ${}^2K$ is the two-particle reduced Hamiltonian matrix [40]. Taking the expectation value of the Hamiltonian yields an expression for the energy

$$E=\sum_{m,n,p,q} {}^2K^{m,n}_{p,q}\,{}^2D^{m,n}_{p,q} \qquad (2)$$

in terms of the 2-RDM

$${}^2D^{m,n}_{p,q}=\langle\Psi|\hat{a}^{\dagger}_m\hat{a}^{\dagger}_n\hat{a}_q\hat{a}_p|\Psi\rangle. \qquad (3)$$

To minimize the energy as a functional of the 2-RDM, however, we require restrictions on the 2-RDM which are both necessary and sufficient for the 2-RDM to correspond to an N-particle wave function. These restrictions are known as N-representability conditions.

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

$$\langle\Phi_i|=\langle\Psi|\hat{C}_i \qquad (4)$$

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

$$M^i_j=\langle\Phi_i|\Phi_j\rangle=\langle\Psi|\hat{C}_i\hat{C}^{\dagger}_j|\Psi\rangle \qquad (5)$$

must be positive semidefinite. A positive semidefinite matrix has all non-negative eigenvalues. We indicate that a matrix has this property by the notation $M\geqslant 0$. For a RDM that corresponds to a wave function these vector-space restrictions are always satisfied. More generally, however, these conditions offer a systematic approach for imposing N-representability conditions on a RDM without using the wave function.

If we choose for each $\hat{C}_i$ a second-quantized operator $\hat{a}^{\dagger}_i$ that creates a particle in the ith orbital, we determine that the one-particle reduced density matrix must be positive semidefinite,

$${}^1D^i_j=\langle\Psi|\hat{a}^{\dagger}_i\hat{a}_j|\Psi\rangle\geqslant 0, \qquad (6)$$

and, if we choose for each $\hat{C}_i$ an operator $\hat{a}_i$ that annihilates a particle in the ith orbital, we discover that the one-hole reduced density matrix must also be positive semidefinite,

$${}^1Q^i_j=\langle\Psi|\hat{a}_i\hat{a}^{\dagger}_j|\Psi\rangle\geqslant 0. \qquad (7)$$

The second-quantized operators may be rearranged according to the anticommutation relation for fermions (+ sign) or the commutation relation for bosons (− sign),

$$\hat{a}_j\hat{a}^{\dagger}_i\pm\hat{a}^{\dagger}_i\hat{a}_j=\delta^i_j . \qquad (8)$$

The relation in Eq. (8) provides a linear mapping between the matrices ${}^1D$ and ${}^1Q$ which depends on whether the particles are bosons or fermions. For fermions the D and Q conditions have sufficient strength to force the eigenvalues of both ${}^1D$ and ${}^1Q$ to lie between 0 and 1. By adding the condition that ${}^1D$ traces to N, we obtain Coleman's N-representability conditions for the fermionic 1-RDM [4,6,35]. For bosons either the D or the Q condition is sufficient. We describe any 1-RDM satisfying both the D and the Q conditions as *1-positive*.

TABLE I. Positivity conditions for the 3-RDM.

$$
\begin{gathered}
{}^{3}D^{i,j,k}_{p,q,r} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}^{\dagger}_{k} \hat{a}_{r} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{3}E^{i,j,k}_{p,q,r} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}_{k} \hat{a}^{\dagger}_{r} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{3}F^{i,j,k}_{p,q,r} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}_{j} \hat{a}_{k} \hat{a}^{\dagger}_{r} \hat{a}^{\dagger}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{3}Q^{i,j,k}_{p,q,r} = \langle \Psi | \hat{a}_{i} \hat{a}_{j} \hat{a}_{k} \hat{a}^{\dagger}_{r} \hat{a}^{\dagger}_{q} \hat{a}^{\dagger}_{p} | \Psi \rangle \geqslant 0
\end{gathered}
$$

TABLE II. Positivity conditions for the 4-RDM.

$$
\begin{gathered}
{}^{4}D^{i,j,k,l}_{p,q,r,s} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}^{\dagger}_{k} \hat{a}^{\dagger}_{l} \hat{a}_{s} \hat{a}_{r} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{4}E^{i,j,k,l}_{p,q,r,s} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}^{\dagger}_{k} \hat{a}_{l} \hat{a}^{\dagger}_{s} \hat{a}_{r} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{4}G^{i,j,k,l}_{p,q,r,s} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}_{k} \hat{a}_{l} \hat{a}^{\dagger}_{s} \hat{a}^{\dagger}_{r} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{4}F^{i,j,k,l}_{p,q,r,s} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}_{j} \hat{a}_{k} \hat{a}_{l} \hat{a}^{\dagger}_{s} \hat{a}^{\dagger}_{r} \hat{a}^{\dagger}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0 \\
{}^{4}Q^{i,j,k,l}_{p,q,r,s} = \langle \Psi | \hat{a}_{i} \hat{a}_{j} \hat{a}_{k} \hat{a}_{l} \hat{a}^{\dagger}_{s} \hat{a}^{\dagger}_{r} \hat{a}^{\dagger}_{q} \hat{a}^{\dagger}_{p} | \Psi \rangle \geqslant 0
\end{gathered}
$$

Consider $\hat{C}$ to be a product of two fundamental second-quantized operators. The resulting basis functions in Eq. (4) may be naturally grouped into three orthogonal vector spaces according to the number of creation operators in $\hat{C}$. Restricting the metric matrix M for each of these spaces to be semidefinite yields three separate conditions. For $\hat{C} \in \{\hat{a}^{\dagger}_{i}\hat{a}^{\dagger}_{j}\}$ we obtain the positivity constraint on the 2-RDM,

$$
{}^{2}D^{i,j}_{p,q} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}^{\dagger}_{j} \hat{a}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0, \tag{9}
$$

and for $\hat{C} \in \{\hat{a}_{i}\hat{a}_{j}\}$ we obtain the positivity constraint on the two-hole RDM,

$$
{}^{2}Q^{i,j}_{p,q} = \langle \Psi | \hat{a}_{i} \hat{a}_{j} \hat{a}^{\dagger}_{q} \hat{a}^{\dagger}_{p} | \Psi \rangle \geqslant 0. \tag{10}
$$

Note that the adjoint of a product of second-quantized operators is the product of the individual adjoints in reverse order, for example, the adjoint of $\hat{a}^{\dagger}_{i}\hat{a}_{j}$ is $\hat{a}^{\dagger}_{j}\hat{a}_{i}$. The final positivity condition arises from selecting $\hat{C}$ to be single-particle excitations or deexcitations, that is, $\hat{C} \in \{\hat{a}^{\dagger}_{i}\hat{a}_{j}, \hat{a}_{i}\hat{a}^{\dagger}_{j}\}$. If we just consider the excitations, $\hat{C} \in \{\hat{a}^{\dagger}_{i}\hat{a}_{j}\}$, we obtain a form of the G condition [5,31–35,41],

$$
{}^{2}G^{i,j}_{p,q} = \langle \Psi | \hat{a}^{\dagger}_{i} \hat{a}_{j} \hat{a}^{\dagger}_{q} \hat{a}_{p} | \Psi \rangle \geqslant 0. \tag{11}
$$

The three matrices ${}^{2}D$, ${}^{2}G$, and ${}^{2}Q$ are linearly related by the commutation relations. It has been shown that the metric matrix from $\hat{C} \in \{\hat{a}_{i}\hat{a}^{\dagger}_{j}\}$ is positive semidefinite if and only if the G matrix is positive semidefinite. However, the matrix arising from the set of operators $\{\hat{a}^{\dagger}_{i}\hat{a}_{j}, \hat{a}_{i}\hat{a}^{\dagger}_{j}\}$ may be slightly more general. We describe any 2-RDM satisfying all of these conditions as *2-positive*.

The conditions that a k-RDM be k-positive follow from writing the $\hat{C}_{i}$ in Eq. (4) as products of k second-quantized operators. As in the two-particle case the resulting basis functions lie in $k+1$ orthogonal vector spaces according to the number of creation operators in the product. Each metric matrix from one of the $k+1$ vector spaces must be positive semidefinite. Furthermore, all of the metric matrices are connected with each other by the anticommutation (fermions) or commutation (bosons) relation in Eq. (8). A k-RDM that is k-positive contracts to a $(k-1)$-RDM that is $(k-1)$-positive. Some conditions for 3-positivity and 4-positivity, given in Tables I and II, respectively, will later be explored numerically. We say that a 2-RDM is k-positive if it arises from the *contraction* of a k-positive k-RDM. The strength of these conditions on the 2-RDM increases rapidly with increasing k. The conditions for 3-positivity have been examined numerically in the work of Erdahl and Jin [28,29], and the importance of the ${}^{4}G$ condition in Table II was recognized by Valdemoro, Tel, and Perez-Romero [21,22].

There are two interwoven perspectives for understanding the k-positivity conditions. By applying polynomials in creation and/or annihilation operators of degree k to the wave function, we generate a vector space in Eq. (4). Restricting the metric of this vector space to be non-negative in Eq. (5) yields the k-positivity conditions. Any operator $\hat{O}$ of degree k in the creation and/or annihilation operators may be generated through a linear combination of the operators $\hat{C}_{i}$ in Eq. (5),

$$
\hat{O} = \sum_{i} \alpha_{i} \hat{C}_{i}. \tag{12}
$$

The operator $\hat{O}\hat{O}^{\dagger}$ must have a non-negative expectation value if it is evaluated with an N-representable RDM. Therefore, for a given k-RDM we have N-representability conditions arising from the fact that the following expectation value must be non-negative:

$$
\langle \Psi | \hat{O}\hat{O}^{\dagger} | \Psi \rangle \geqslant 0 \tag{13}
$$

for all operators $\hat{O}$ of degree k. To understand the relationship of these conditions to k-positivity, we insert Eq. (12) into Eq. (13) to obtain

$$
\sum_{i,j} \alpha_{i} \alpha^{*}_{j} \langle \Psi | \hat{C}_{i} \hat{C}^{\dagger}_{j} | \Psi \rangle \geqslant 0, \tag{14}
$$

which with the definition for the metric matrix in Eq. (5) is

$$
\sum_{i,j} \alpha_{i} M^{i}_{j} \alpha^{*}_{j} \geqslant 0. \tag{15}
$$

However, Eq. (15) is just the expectation value of the metric matrix M with respect to the vector α whose components are α_{i}. The minimum of the left side in Eq. (15) is achieved when we select α to be the lowest eigenvector of M. Equation (15) is thus valid if and only if the metric matrix M is positive semidefinite. Therefore, the N-representability conditions that arise from constraining the expectation value of $\hat{O}\hat{O}^{\dagger}$ to be non-negative for all operators $\hat{O}$ of degree k are equivalent to the metric conditions that we call k-positivity. Equations (5) and (13) offer two complementary definitions for k-positivity.

We now demonstrate mathematically that a 4-positive RDM provides a four-quasiparticle model for many-body quantum mechanics in which the generalized uncertainty relation is completely satisfied for *all* pairs of operators with no more than two-particle interactions. An arbitrary operator $\hat{O}$ may be expressed in terms of two Hermitian operators:

$$\hat{O}=\hat{A}+i\hat{B}. \tag{16}$$

Consider the subset of operators $\hat{O}$ with vanishing expectation values

$$\hat{O}_0(x,y)=x(\hat{A}-\langle\hat{A}\rangle)+iy(\hat{B}-\langle\hat{B}\rangle), \tag{17}$$

where the real variables x and y affect only the normalization of the operators $\hat{A}$ and $\hat{B}$, respectively. For a succinct derivation the wave function is omitted from the notation for the expectation value. We restrict our attention to those operators $\hat{O}$, $\hat{A}$, and $\hat{B}$ of degree 4 in the creation and/or annihilation operators. This restriction allows us to evaluate the expectation value in Eq. (13) with only a knowledge of the 4-RDM. As defined earlier, the 4-RDM is said to be 4-positive if and only if Eq. (13) is valid for all operators $\hat{O}$ of degree 4 in the creation and/or annihilation operators. Thus, if we assume that the 4-RDM is 4-positive, then for all operators $\hat{O}_0(x,y)$ we have

$$\langle\hat{O}_0(x,y)\hat{O}_0(x,y)^\dagger\rangle\geqslant 0. \tag{18}$$

Rewriting Eq. (18) more explicitly, we have a function of x and y that must be non-negative:

$$(x\ \ y)\begin{pmatrix}\langle(\hat{A}-\langle\hat{A}\rangle)^2\rangle & -\frac{i}{2}\langle[\hat{A},\hat{B}]\rangle\\ -\frac{i}{2}\langle[\hat{A},\hat{B}]\rangle & \langle(\hat{B}-\langle\hat{B}\rangle)^2\rangle\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}\geqslant 0. \tag{19}$$

This function will be non-negative for all x and y if and only if the 2×2 matrix is positive semidefinite, that is, both of its eigenvalues must be non-negative. It follows that the product of the eigenvalues (the determinant of the 2×2 matrix) must be non-negative:

$$\langle(\hat{A}-\langle\hat{A}\rangle)^2\rangle\langle(\hat{B}-\langle\hat{B}\rangle)^2\rangle\geqslant-\frac{1}{4}\langle[\hat{A},\hat{B}]\rangle^2. \tag{20}$$

For the function in Eq. (19) to be real, we must have that the $\langle[\hat{A},\hat{B}]\rangle$ is purely imaginary. Thus, Eq. (20) may be cast in its more familiar form,

$$\langle(\hat{A}-\langle\hat{A}\rangle)^2\rangle^{1/2}\langle(\hat{B}-\langle\hat{B}\rangle)^2\rangle^{1/2}\geqslant\frac{1}{2}|\langle[\hat{A},\hat{B}]\rangle|. \tag{21}$$

This is the *uncertainty relation* for two-particle operators. Note that the uncertainty relations, like the positivity condition in Eq. (18) from which they arise, are automatically satisfied when we evaluate the expectation values with respect to an N-particle wave function. However, when the expectation value is evaluated via a 4-RDM, which may not be N-representable, the uncertainty relations like the positivity conditions serve as strong N-representability conditions. These arguments may be generalized to k-positive RDMs and operators with $k/2$-particle interactions. An operator with $k/2$-particle interactions is defined as the product of k creation or annihilation operators. Consequently: *If a k-RDM is k-positive, then the uncertainty relations hold for all Hermitian operators with no more than k/2-particle interactions.*

III. DISPERSION CONDITION

In second quantization the contracted Schrödinger equation may be derived by testing the N-particle Schrödinger equation with all two-particle excitations from the exact wave function [13,20],

$$\langle\Phi^{i,j}_{k,l}|\hat{H}\Psi\rangle=E\langle\Phi^{i,j}_{k,l}|\Psi\rangle, \tag{22}$$

where

$$\langle\Phi^{i,j}_{k,l}|=\langle\Psi|\hat{a}^\dagger_i\hat{a}^\dagger_j\hat{a}_l\hat{a}_k. \tag{23}$$

Using Eqs. (1) and (23), we can write the CSE in Eq. (22) in terms of the reduced Hamiltonian ${}^2K$ and the ${}^4G$ matrix from Table II,

$$\sum_{m,n,p,q}{}^4G^{i,j,k,l}_{m,n,p,q}\,{}^2K^{m,n}_{p,q}=E\,{}^2D^{i,j}_{k,l}. \tag{24}$$

In the customary formulation of the CSE the second-quantized operators in ${}^4G$ are rearranged to express ${}^4G$ in terms of the 2-, 3-, and 4-RDMs [13,15,20]. By moving the energy into the sum on the left side of Eq. (24), we can also write the CSE as

$$\sum_{m,n,p,q}{}^4G^{i,j,k,l}_{m,n,p,q}\,{}^2\tilde{K}^{m,n}_{p,q}=0, \tag{25}$$

where the energy-shifted reduced Hamiltonian ${}^2\tilde{K}^{m,n}_{p,q}$

$${}^2\tilde{K}^{m,n}_{p,q}={}^2K^{m,n}_{p,q}-E/[N(N-1)]\delta^m_p\delta^n_q \tag{26}$$

lies in the null space of ${}^4G$.

The dispersion condition for the Hamiltonian has the form

$$\langle\Psi|(\hat{H}-E)^2|\Psi\rangle=0. \tag{27}$$

If restricted to a set of *pure* N-representable RDMs, both the CSE and the dispersion condition are equivalent, and their RDM (or ${}^4G$) solutions correspond to wave-function solutions of the Schrödinger equation [13,27]. As shown in previous work [13], if we multiply the CSE in Eq. (25) by ${}^2K^{i,j}_{k,l}$ and sum over the indices i, j, k, and l, we obtain Eq. (27) in terms of the reduced Hamiltonian and the ${}^4G$ matrix. This proves that the CSE always implies the dispersion condition even if ${}^4G$ is not N-representable. By deriving the CSE from Eq. (27) through the Hellmann-Feynman theorem [42], we now consider whether the dispersion condition implies the CSE without additional N-representability conditions.

Although previous derivations of the CSE [13] have employed test functions as in Eq. (23), the CSE may also be derived from the dispersion condition by applying the Hellmann-Feynman theorem. The Hellmann-Feynman theorem states that the first derivative of the energy, independent of the first derivatives of the wave function, depends only on the expectation value of the first derivative of the Hamiltonian [42]. Because the Hamiltonian is self-adjoint, the dispersion relation in Eq. (27) may also be written as

$$\langle \Psi | (\hat{H} - E)(\hat{H} - E)^{\dagger} | \Psi \rangle = 0. \tag{28}$$

Through the Hellmann-Feynman theorem we differentiate Eq. (28) with respect to a parameter in the Hamiltonian to produce

$$\langle \Psi | (\hat{H}' - E')(\hat{H} - E) + (\hat{H} - E)[(\hat{H}^{\dagger})' - E'] | \Psi \rangle = 0. \tag{29}$$

By using the facts that the derivative of the energy is a constant and that the expectation value of $(\hat{H} - E)$ vanishes, we may simplify Eq. (29) to obtain

$$\langle \Psi | \hat{H}'(\hat{H} - E) + (\hat{H} - E)(\hat{H}^{\dagger})' | \Psi \rangle = 0. \tag{30}$$

Any element of the reduced Hamiltonian ${}^2K^{i,j}_{k,l}$ may be written in terms of a real part ϵ_r and an imaginary part ϵ_i,

$${}^2K^{i,j}_{k,l} = \epsilon_r + \epsilon_i . \tag{31}$$

If the Hamiltonian parameter is chosen to be ϵ_r, then

$$\frac{\partial \hat{H}}{\partial \epsilon_r} = \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k , \tag{32}$$

$$\frac{\partial (\hat{H}^{\dagger})}{\partial \epsilon_r} = \hat{a}_k^{\dagger} \hat{a}_l^{\dagger} \hat{a}_j \hat{a}_i , \tag{33}$$

and Eq. (30) becomes

$$\langle \Phi^{i,j}_{k,l} | (\hat{H} - E) | \Psi \rangle + \langle \Psi | (\hat{H} - E) | \Phi^{i,j}_{k,l} \rangle = 0. \tag{34}$$

If the Hamiltonian parameter is chosen to be ϵ_i, then

$$\frac{\partial \hat{H}}{\partial \epsilon_i} = \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k , \tag{35}$$

$$\frac{\partial (\hat{H}^{\dagger})}{\partial \epsilon_i} = - \hat{a}_k^{\dagger} \hat{a}_l^{\dagger} \hat{a}_j \hat{a}_i , \tag{36}$$

and Eq. (30) becomes

$$\langle \Phi^{i,j}_{k,l} | (\hat{H} - E) | \Psi \rangle - \langle \Psi | (\hat{H} - E) | \Phi^{i,j}_{k,l} \rangle = 0. \tag{37}$$

Addition of Eqs. (34) and (37) yields the CSE

$$\langle \Phi^{i,j}_{k,l} | (\hat{H} - E) | \Psi \rangle = 0. \tag{38}$$

In the derivation of the dispersion condition from the CSE we employ only multiplication and summation, but in the above derivation of the CSE from Eq. (28) we implicitly employ an additional N-representability condition when we differentiate via the *Hellmann-Feynman* theorem. The differentiation of the dispersion condition with respect to ${}^2K$ is equivalent to applying Hellmann-Feynman forces to the system along each element of ${}^2K$. Therefore, the CSE is a stronger N-representability condition than Eq. (28) because it correctly accounts for local perturbations about the dispersion condition in accordance with the Hellmann-Feynman theorem.

When the RDMs are kept N-representable, the solutions of the CSE and the dispersion condition are equivalent, and they correspond to wave-function solutions of the N-particle Schrödinger equation. Are the CSE and the dispersion condition only the same when complete N-representability is applied, or is there an approximate set of N-representability conditions which can make these two reduced formulations of the problem equivalent? To answer this question, we consider the N-representability conditions that arise from forcing the metric matrix ${}^4G$ in Table II to be positive semidefinite. Keeping ${}^4G$ positive semidefinite means Eq. (13) will be satisfied for any operator $\hat{O}$ that is a linear combination of operators from the set $\{\hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k\}$. Furthermore, the *dispersion* associated with such an operator $\hat{O}$, that is, the expectation value of $(\hat{O} - \langle \Psi | \hat{O} | \Psi \rangle)^2$, will be non-negative. Because Ψ is an eigenstate of the Hamiltonian H, the dispersion of H vanishes as in Eq. (28). Consider the dispersion associated with the perturbed Hamiltonian $\hat{H}_p$,

$$\hat{H}_p = \hat{H} - E + \epsilon \hat{\Gamma}, \tag{39}$$

where $\hat{\Gamma}$ is the two-particle excitation operator

$$\hat{\Gamma} = \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_l \hat{a}_k . \tag{40}$$

The dispersion relation for $\hat{H}_p$ is

$$\langle \Psi | (\hat{H} - E + \epsilon \hat{\Gamma})(\hat{H} - E + \epsilon^{\dagger} \hat{\Gamma}^{\dagger}) | \Psi \rangle \geqslant 0. \tag{41}$$

Rearranging the equation into powers of the perturbation ϵ, we have

$$\langle \Psi | (\hat{H} - E)^2 | \Psi \rangle + \epsilon \langle \Phi^{i,j}_{k,l} | (\hat{H} - E) | \Psi \rangle + \epsilon^* \langle \Psi | (\hat{H} - E) | \Phi^{i,j}_{k,l} \rangle + |\epsilon|^2 \langle \Psi | \hat{\Gamma} \hat{\Gamma}^{\dagger} | \Psi \rangle \geqslant 0. \tag{42}$$

By Eq. (27) the first term in Eq. (42) is zero. Furthermore, the final term in Eq. (42) is non-negative for any ϵ. We can choose $|\epsilon|$ to be small enough to make this second-order term negligible. If we choose ϵ to be real and $|\epsilon| \ll 1$, then Eq. (42) becomes

$$\epsilon \langle \Phi^{i,j}_{k,l} | (\hat{H} - E) | \Psi \rangle + \epsilon \langle \Psi | (\hat{H} - E) | \Phi^{i,j}_{k,l} \rangle \geqslant 0. \tag{43}$$

Equation (43) can be valid for positive and negative values of ϵ if and only if the coefficient of ϵ vanishes, that is, the ‘‘symmetric’’ CSE in Eq. (34) must be valid. Choosing ϵ equal to $i\gamma$ where γ is real and $|\epsilon| \ll 1$, we can express Eq. (42) as

TABLE III. Accuracy of the correlation energy: 4-positivity vs the wave function.

System		FCI correlation energy	% of correlation energy					
			Wave-function methods					RDM method
N	V		SDCI	SDTQCI	MP2	MP4	CCSD	4-Pos
10	0.8	−0.0384	85.5	98.85	92.57	99.703	101.07	100.000103
30	0.8	−0.0130	79.0	95.94	85.1	96.43	101.08	100.0000670
75	0.8	−0.00526	76.5	94.25	82.3	94.5	100.642	100.0000113
10	1.6	−0.186	59.9	88.9	76.6	100.224	no solution	100.0958
30	1.6	−0.128	27.9	47.5	35.2	53.9	no solution	101.90
75	1.6	−0.117	11.8	20.9	14.8	23.6	no solution	100.428

$$\gamma\langle\Phi^{i,j}_{k,l}|(\hat{H}-E)|\Psi\rangle-\gamma\langle\Psi|(\hat{H}-E)|\Phi^{i,j}_{k,l}\rangle\geqslant 0. \qquad (44)$$

Equation (44) can be valid for positive and negative values of γ if and only if the coefficient of γ vanishes, that is, the ‘‘antisymmetric’’ CSE in Eq. (37) must be valid. Addition of Eqs. (34) and (37) yields the CSE.

With the N-representability condition ${}^4G\geqslant 0$ the dispersion condition and the CSE have a common set of RDM solutions. Because Eqs. (34) and (37) are the Hellmann-Feynman derivatives of the dispersion condition with respect to real and imaginary components of the reduced Hamiltonian, respectively, we have also proved that the nonnegativity condition ${}^4G\geqslant 0$ is sufficient to prove the Hellmann-Feynman theorem for the operator $(\hat{H}-E)^2$. The traditional proof of the Hellmann-Feynman theorem [42] requires an application of the N-particle Schrödinger equation. At an early conference on RDMs, Erdahl and Garrod [43] employed the ${}^2G$ positivity condition to connect the dispersion condition and a simplified CSE for noninteracting N-particle Hamiltonians. Each of the present authors independently extended this earlier result to the interacting CSE and ${}^4G$ [29,44]. The positivity of ${}^4G$ provides precisely the N-representability conditions that are necessary to make the CSE and the dispersion condition equivalent.

IV. APPLICATION

To illustrate the strength of the representability conditions, we employ a many-body system of bosons. Consider N bosons in the ground state of a two-level system where the energy levels are at -1 and $+1$. To this noninteracting system, we add a perturbation that acts to switch two bosons from the ground state to the excited state. The mean-field energy equals -1 for all N. Mazziotti and Herschbach have employed the model to explore reduced Hamiltonian interpolation [38,39]. Additional details of the model may be found in these works. The bosonic system may also be converted into a fermionic system through the introduction of a second quantum number (often called a ‘‘color’’ variable) which assumes N values (or ‘‘colors’’) for each level ($+1$ or -1) so that each particle occupies a different, albeit degenerate, state. The resulting quasispin system of fermions was originally employed by Lipkin to investigate fermionic correlation phenomena [37], and, more recently, Mazziotti has used the fermionic version to investigate the contracted Schrödinger equation [13–15,23].

A set of N-representability conditions on the 2-RDM has been developed for minimizing the energy in Eq. (2). To illustrate the strength of 3- and 4-positivity, we employ the conditions in Tables I and II, respectively. As we mentioned earlier, these conditions do not completely exhaust the metric conditions associated with 3- and 4-positivity. However, even the application of these conditions is challenging, and the authors are not aware of previous calculations using any of these conditions other than the positivity of the 4-RDM [13]. The energy in Eq. (2) is evaluated by contracting the 3- and 4-RDMs to the 2-RDM. Through constrained optimization the energy is minimized while the lowest eigenvalues of the matrices in Table I (3-positivity) or Table II (4-positivity) are constrained to be non-negative. The algorithm employs sequential quadratic programming for the constrained optimization and computes the lowest eigenvalues through standard diagonalization.

The strength of 4-positivity for the 2-RDM is demonstrated through comparisons of the method with standard wave-function and many-body perturbation techniques. We present data for moderate to large particle numbers, $N=10$, 30, and 75, and for moderate and strong interactions, $V=0.8$ and 1.6. Table III gives the percentage of the correlation energy (CE) achieved (three significant figures are reported for the deviation of the result from 100%), and Table IV gives the error in the 2-RDM as measured by the infinity norm (the column MF denotes results for the mean field). For moderate interactions minimization of the energy with 4-positivity conditions (4-Pos) yields the CE within 0.0001% in Table III, which is four orders of magnitude more accurate than the value obtained using single-double coupled-cluster (CCSD) equations; for strong interactions ($V=1.6$) 4-positivity yields the CE with less than 2% error while the CCSD equations have no solution for $V\geqslant 1$. The comparisons of 4-positivity with fourth-order many-body perturbation theory (MP4) are even more dramatic because for strong interactions MP4 captures less than half of the CE. We also report results from configuration-interaction wave functions, including single and double excitations (SDCI) and single, double, triple, and quadruple excitations (SDTQCI), and second-order perturbation theory (MP2). These traditional

TABLE IV. Accuracy of the 2-RDM: 4-positivity vs the wave function.

System		2-RDM error ×100						
		Wave-function methods						RDM method
N	*V*	MF	SDCI	SDTQCI	MP2	MP4	CCSD	4-Pos
10	0.8	9.19	5.16	0.572	1.41	0.0660	0.554	0.0161
30	0.8	3.68	5.30	0.712	1.22	0.435	0.221	0.000669
75	0.8	1.62	5.83	0.791	0.654	0.302	0.0602	0.00344
10	1.6	35.2	22.7	10.3	13.0	4.31	no solution	0.334
30	1.6	46.5	35.9	32.4	39.3	29.0	no solution	0.321
75	1.6	49.5	39.6	39.7	46.7	42.1	no solution	0.223

approaches are less accurate than 4-positivity by many orders of magnitude.

The rate of convergence with the order *k* of positivity is shown in Table V. The results for 2-, 3-, and 4-positivity (columns headed 2-Pos, 3-Pos, and 4-Pos) reveal a dramatic change in accuracy when 2-positivity is replaced with 3-positivity. In some cases the addition of 4-positivity yields only marginal improvements. In the worst case for the density-matrix method, when $N=30$ and $V=1.6$, 3-positivity yields the CE within 3%, and 4-positivity improves this result to 2%. In the columns marked $D2$, $D3$, and $D4$, calculations are performed by constraining just the 2-RDM, 3-RDM, or 4-RDM to be positive semidefinite (the *D* condition alone). Because these calculations overestimate the CE by factors as large as 50, they emphasize the importance of the combined strength of various positivity conditions for achieving an accurate modeling of correlation phenomena without the wave function.

Correlation energies obtained by using the dispersion condition and the CSE are compared in Table VI. We solve for the 4-RDM that satisfies the CSE or the dispersion condition subject to an *N*-representability condition, the positive semidefiniteness of either ^4D or ^4G. Theoretically, we have shown that the dispersion condition is weaker than the CSE if the matrix ^4G is not positive semidefinite, but with the ^4G positivity the dispersion condition and the CSE have equivalent solutions. Results in Table VI demonstrate that the CSE with $^4D\geqslant 0$ (also computed in Ref. [19]) is much more accurate than the dispersion condition with $^4D\geqslant 0$. In fact, the dispersion condition does not significantly improve the 4-RDM positivity results reported in Table V under the column $D4$. Unlike the dispersion condition, the CSE is implicitly imposing a portion of the ^4G positivity restriction. By contrast, solving the dispersion condition with $^4G\geqslant 0$ gives highly accurate energies which are equivalent to those obtained by solving the CSE with $^4G\geqslant 0$. The importance of the *G* condition lies not only in that it makes the dispersion condition and the CSE equivalent but also in that it enforces the uncertainty relations for particle-conserving operators like the Hamiltonian.

V. DISCUSSION AND CONCLUSIONS

The relationship between constraining the metric matrices to be positive semidefinite and enforcing the uncertainty relations has been elucidated. Previous calculations, using the two-particle *D*, *Q*, and *G* conditions (2-positivity), imposed the uncertainty relations for only many-body operators without interactions [31,32,34]. The conditions of 2-positivity are necessary and sufficient for determining the energies of noninteracting *N*-particle Hamiltonians. The complete 4-positivity conditions enforce the uncertainty relations for *all* operators with two-particle interactions. Whether the 4-positivity conditions will allow us to compute the exact energies from *N*-particle Hamiltonians with no more than two-particle interactions is an open question. Unlike the operators without interactions, the operators with pairwise interactions can exhibit an extremely large degree of correlation. The calculations in this work, employing an important subset (given in Table II) of the 4-positivity restrictions, indicate that the 4-positivity restrictions are strong enough to

TABLE V. Convergence of correlation energy with *k*-positivity.

System		Correlation energy	% of correlation energy for RDM methods					
N	*V*		D2	D3	D4	2-Pos	3-Pos	4-Pos
10	0.8	−0.0384	731	376	264	731	100.0376	100.000103
30	0.8	−0.0130	2165	1114	783	2165	100.0103	100.0000670
75	0.8	−0.00526	5338	2746	1931	5238	100.00167	100.0000113
10	1.6	−0.186	478	255	195	478	101.85	100.0958
30	1.6	−0.128	707	377	288	707	102.86	101.90
75	1.6	−0.117	758	404	309	758	100.644	100.428

TABLE VI. Accuracy of the correlation energy: Dispersion relation vs CSE.

System		FCI correlation energy	% of correlation energy			
			Dispersion relation		CSE	
N	V		$D4$	$G4$	$D4$	$G4$
10	0.8	−0.0384	260	99.9856	116.5	99.9856
30	0.8	−0.0130	632	99.9860	149.8	99.9860
75	0.8	−0.00526	1357	99.9092	103.10	99.9092
10	1.6	−0.186	168.2	100.0336	123.3	100.0336
30	1.6	−0.128	234	100.486	125.8	100.486
75	1.6	−0.117	245	99.9657	115.2	99.9657

obtain accurate energies in systems with very high correlation.

The connections that exist among the dispersion condition, the CSE, and the metric *N*-representability conditions are an important part of the synthesis of variational minimization and the CSE. The dispersion condition and the CSE share an important property: either one is a necessary and a sufficient condition that a *pure* *N*-representable RDM derives from a wave function which satisfies the Schrödinger equation (Nakatsuji's theorem). With partial *N*-representability conditions (such as ${}^4D \geqslant 0$), however, the CSE is significantly more powerful than the dispersion condition. Results in Table VI show that the CSE with ${}^4D \geqslant 0$ is far more accurate than dispersion with ${}^4D \geqslant 0$. The CSE enforces Hellmann-Feynman perturbations of the dispersion condition which are implicitly associated with the condition ${}^4G \geqslant 0$. It is this feature rather than Nakatsuji's theorem that distinguishes the CSE from the dispersion condition when only approximate *N*-representability conditions are imposed. For this reason cumulant reconstruction for solving the CSE is not easily extended to the dispersion condition even though both equations satisfy Nakatsuji's theorem. The condition ${}^4G \geqslant 0$ contains *all* of the *N*-representability conditions that are necessary to make the CSE and the dispersion condition equivalent. Because the four-particle *G* condition implicitly conveys the most important information in the CSE, the part of the CSE that is independent of the dispersion condition, it allows us through the more general notion of 4-positivity to minimize the energy directly *without* the CSE.

Many processes in chemistry and physics from ordinary bond stretching to superconductivity are not readily treated by conventional implementations of many-body perturbation theory or coupled-cluster theory [45]. Often these situations require multireference treatments or even full configuration interaction (FCI). Since the storage for a FCI calculation scales exponentially with the number of electrons, its application is restricted to small molecules. Energy minimization with 4-positivity, a nonperturbative approach to electronic structure, also has the ability to treat static correlation effectively where the scaling of either the 2-RDM or the 4-RDM ($r^2 \times r^2$ and $r^4 \times r^4$, respectively where r is the rank of the one-particle basis set) is much more reasonable than the scaling of the FCI wave function. Although the CSE with functional reconstruction also determines the 2-RDM without the wave function, the present calculations indicate that the *cumulant* reconstruction as a renormalized perturbation theory is not capable of treating highly correlated quantum systems as accurately as energy minimization of the CSE with 4-positivity [14,23]. Further reduction in computational effort may be possible by constraining only the most important parts of the metric matrices to be positive semidefinite; the effectiveness of any reduction will depend upon the nature of the quantum system and the strength of the correlation. Valdemoro, Tel, and Perez-Romero have recently proposed several constraints upon the elements of the 2-RDM which are implied by the condition that the ${}^4G$ matrix be non-negative [21].

The quality of the energies from 4-positivity challenges us to develop both existing and additional mathematical machinery to enforce these conditions efficiently. Effective FCI algorithms have been under construction for many years [46] with important improvements occurring recently [47], but the application of the mathematical techniques to the minimization of the energy subject to 4-positivity constraints is a frontier that requires both theoretical and computational exploration. Recent techniques for positive semidefinite programming, anticipated by earlier research in the RDM literature [34], may facilitate the development of improved 4-positivity algorithms that are capable of treating atoms and molecules effectively [48].

Approaches to many-body correlation may generally be arranged in two categories, upper-bound variational approximations and perturbation techniques. The 4-positivity restrictions on the 2-RDM offer an approach to many-particle correlation with several distinguishing features: (i) the calculation of a tight lower bound to the *N*-body energy, (ii) the use of nonperturbative positivity restrictions which provide a robust method for accuracy at all perturbation strengths, and (iii) the direct determination of the 2-RDM without the *N*-particle wave function. The nonperturbative nature of the density-matrix approach manifests itself in the determination of correlation energies in Table III that are more accurate than those from wave-function methods. The last feature responds to Coulson's after-dinner challenge to determine a useful description for the set of ensemble *N*-representable 2-RDMs. Earlier studies [31–34] of *N*-representability employed at most 2-positivity and overestimated the correlation energy by large factors. By constraining the 2-RDM to obey the uncertainty relations for operators with two-particle interactions, we have obtained for ground-state correlation phenomena an accurate mapping of quantum mechanics onto four particles. We observe rapid convergence of the correlation energy with the order of positivity; specifically, there is a significant jump in accuracy between 2- and 3-positivity which we associate with the onset of correlated operators in the uncertainty relations. Although computationally challenging, the direct energy minimization with 3- or 4-positivity will eventually provide tools for areas of chemistry and physics dominated by correlation such as bond stretching, molecular dissociation, transition-metal phenomena, weak intermolecular interactions, and superconductivity.

ACKNOWLEDGMENTS

We express our appreciation to Professor A. J. Coleman, Professor D. R. Herschbach, and Dr. A. Mazziotti for their encouragement of our efforts to understand *N*-representability. We also gratefully acknowledge both the NSF and the NSERC for their generous support.

---

[1] C. A. Coulson, Rev. Mod. Phys. **32**, 175 (1960).
[2] K. Husimi, J. Phys. Soc. Jpn. **22**, 264 (1940); P. O. Löwdin, Phys. Rev. **97**, 1474 (1955); J. E. Mayer, *ibid.* **100**, 1579 (1955).
[3] R. H. Tredgold, Phys. Rev. **105**, 1421 (1957); Y. Mizuno and T. Izuyama, Prog. Theor. Phys. **18**, 33 (1957); R. U. Ayres, Phys. Rev. **111**, 1453 (1958); F. Bopp, Z. Phys. **156**, 1421 (1959).
[4] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[5] C. Garrod and J. Percus, J. Math. Phys. **5**, 1756 (1964).
[6] A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer-Verlag, New York, 2000).
[7] F. Colmenero, C. Perez del Valle, and C. Valdemoro, Phys. Rev. A **47**, 971 (1993).
[8] F. Colmenero and C. Valdemoro, Phys. Rev. A **47**, 979 (1993).
[9] F. Colmenero and C. Valdemoro, Int. J. Quantum Chem. **51**, 369 (1994).
[10] H. Nakatsuji and K. Yasuda, Phys. Rev. Lett. **76**, 1039 (1996).
[11] K. Yasuda and H. Nakatsuji, Phys. Rev. A **56**, 2648 (1997).
[12] C. Valdemoro, L. M. Tel, and E. Perez-Romero, Adv. Quantum Chem. **28**, 33 (1997).
[13] D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998).
[14] D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998).
[15] D. A. Mazziotti, Int. J. Quantum Chem. **70**, 557 (1998).
[16] C. Valdemoro, M. P. de Lara-Castells, E. Perez-Romero, and L. M. Tel, Adv. Quantum Chem. **31**, 37 (1999).
[17] K. Yasuda, Phys. Rev. A **59**, 4133 (1999).
[18] E. Ehara, M. Nakata, H. Kou, K. Yasuda, and H. Nakatsuji, Chem. Phys. Lett. **305**, 483 (1999).
[19] D. A. Mazziotti, Phys. Rev. A **60**, 3618 (1999).
[20] D. A. Mazziotti, Phys. Rev. A **60**, 4396 (1999).
[21] C. Valdemoro, L. M. Tel, and E. Perez-Romero, Phys. Rev. A **61**, 032507 (2000).
[22] C. Valdemoro, L. M. Tel, and E. Perez-Romero in *Many-Electron Densities and Density Matrices*, edited by J. Cioslowski (Kluwer, Boston, 2000).
[23] D. A. Mazziotti, Chem. Phys. Lett. **326**, 212 (2000).
[24] D. A. Mazziotti in *Many-Electron Densities and Density Matrices* (Ref. [22]).
[25] S. Cho, Annu. Rep. Gumma Univ. **11**, 1 (1962).
[26] L. Cohen and C. Frishberg, Phys. Rev. A **13**, 927 (1976).
[27] H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[28] R. M. Erdahl and B. Jin, J. Mol. Struct.: THEOCHEM **527**, 207 (2000).
[29] R. M. Erdahl and B. Jin, in *Many-Electron Densities and Density Matrices* (Ref. [22]).
[30] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
[31] C. Garrod, V. Mihailović, and M. Rosina, J. Math. Phys. **10**, 1855 (1975).
[32] C. Garrod and M. A. Fusco, Int. J. Quantum Chem. **10**, 495 (1976).
[33] R. M. Erdahl, Int. J. Quantum Chem. **13**, 697 (1978).
[34] R. Erdahl, Rep. Math. Phys. **15**, 147 (1979).
[35] A. J. Coleman, in *The Force Concept in Chemistry*, edited by E. Deb (Prentice-Hall, New York, 1981).
[36] J. E. Harriman, Phys. Rev. A **30**, 19 (1984).
[37] H. J. Lipkin, N. Meshkov, and A. J. Glick, Nucl. Phys. B **62**, 188 (1965).
[38] D. A. Mazziotti and D. R. Herschbach, Phys. Rev. Lett. **83**, 5185 (1999).
[39] D. A. Mazziotti and D. R. Herschbach, Phys. Rev. A **62**, 043603 (2000).
[40] D. Ter Haar, Rep. Prog. Phys. **24**, 304 (1961).
[41] A. Golebiewski and M. Witko, Phys. Rev. A **38**, 2715 (1988).
[42] R. P. Feynman, Phys. Rev. **56**, 340 (1939).
[43] R. M. Erdahl and C. Garrod, in *Reduced Density Operators with Applications to Physical and Chemical Systems II*, Queens Papers in Pure and Applied Mathematics No. 44, edited by R. M. Erdahl (Queens University Press, Kingston, ON, 1974).
[44] D. A. Mazziotti (unpublished).
[45] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, 2nd ed. (Dover, New York, 1996).
[46] I. Shavitt, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum Press, New York, 1977).
[47] C. D. Sherrill and H. F. Schaefer, Adv. Quantum Chem. **34**, 143 (1999).
[48] L. Vandenberghe and S. Boyd, SIAM Rev. **38**, 49 (1996).