

Quantum Chemistry without Wave Functions: Two-Electron Reduced Density Matrices

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ABSTRACT

For 50 years, progress toward the direct calculation of the ground-state two-electron reduced density matrix (2-RDM) was stymied from an inability to constrain the 2-RDM to represent an N -electron wave function. Recent advances in theory and optimization have realized the direct calculation of the 2-RDM. A variational 2-RDM procedure, using first-order semidefinite programming, has been shown to capture multireference correlation effects important at nonequilibrium geometries [Mazziotti, *Phys. Rev. Lett.* **2004**, 93, No. 213001]. This method emerged from research on a nonvariational calculation of the 2-RDM by the contracted Schrödinger equation. Both approaches will be discussed and illustrated.

1. Introduction

The ground-state energy of a many-electron atom or molecule may be estimated by minimizing the expectation value of the Hamiltonian with respect to a trial wave function with adjustable parameters. By the Rayleigh–Ritz variational principle, the energy estimate from a trial wave function will be an upper bound on the exact ground-state energy. In the early days of quantum chemistry, the judicious design of trial wave functions was practically a “contest” to obtain the best upper bounds on the exact energy.

In 1927, Landau¹ and von Neumann² introduced the *density matrix* into quantum mechanics. The density matrix for the N -electron ground-state wave function, $\Psi(1,2,\dots,N)$, where the numbers represent the spatial and spin coordinates for each electron is given by

$${}^N\mathbf{D}(1,2,\dots,N;1',2',\dots,N') = \Psi(1,2,\dots,N)\Psi^*(1',2',\dots,N'). \quad (1)$$

Integrating the N -electron density matrix over coordinates 3 to N generates the *two-electron reduced density matrix* (2-RDM)

$${}^2\mathbf{D}(1,2;1',2') = \int \Psi(1,2,\dots,N)\Psi^*(1',2',\dots,N) d3\dots dN. \quad (2)$$

Because electrons are indistinguishable with only pairwise interactions, the energy of any atom or molecule may be expressed as a linear functional of the 2-RDM.^{3,4} Formu-

lating the energy as a linear functional of the 2-RDM, however, suggests the tantalizing possibility of employing the 2-RDM rather than the many-electron wave function to compute the ground-state energy of atoms and molecules. In 1955, Mayer⁴ performed an encouraging pencil-and-paper calculation, but Tredgold⁵ soon discovered that the energy for a simple system from a trial 2-RDM could be optimized substantially *below the exact ground-state energy*. Why did the Rayleigh–Ritz variational principle not hold for the 2-RDM expression of the energy? Tredgold,⁵ Coleman,⁶ Coulson,⁷ and others realized that for an N -electron problem the trial 2-RDM was assuming a form that did not correspond to an N -electron wave function; that is, the trial 2-RDM at the minimum energy could not be obtained from the integration of an N -electron density matrix. The 2-RDM must be constrained by additional rules (or conditions) to derive from an N -electron wave function. Coleman described these necessary and sufficient rules as *N -representability conditions*.⁶

The unsuccessful back-of-the-envelope 2-RDM calculations of Coleman and Tredgold already employed four basic requirements for a density matrix of indistinguishable fermions:⁶ the matrix should be (i) normalized to conserve particle number, (ii) Hermitian, (iii) antisymmetric under particle exchange, and (iv) positive semidefinite to keep probabilities nonnegative. A matrix is *positive semidefinite* if and only if all of its eigenvalues are nonnegative. These conditions are sufficient to guarantee that the 2-RDM is a density matrix but not sufficient for the matrix to be representable by an N -electron density matrix, or *N -representable*. What additional conditions must be imposed on a 2-RDM to restrict it to be *N -representable*? While considerable research effort was initially made to understand these conditions, interest in the 2-RDM approach to many-electron atoms and molecules began to wane as the *N -representability problem* appeared intractable.

Interest in the 2-RDM and its *N -representability* returned in the 1990s with the direct calculation of the ground-state 2-RDM without the many-electron wave function from a self-consistent solution of the contracted Schrödinger equation.^{8–15} Recent progress has revealed the importance of a class of *N -representability constraints*, called *positivity conditions*.^{16,17} Erdahl and Jin¹⁶ and Mazziotti and Erdahl¹⁷ generalized these conditions, originally discussed by Coleman⁶ and Garrod and Percus,¹⁸ to a hierarchy of *N -representability conditions*, and Mazziotti and Erdahl¹⁷ showed that each level of the hierarchy corresponds to enforcing the generalized uncertainty relations for a class of operators. With the positivity conditions, the ground-state energy of many-electron atoms and molecules can be accurately computed through a variational calculation in which the energy is directly parametrized as a linear functional of the 2-RDM.

Two approaches to the calculation of the ground-state 2-RDM will be discussed in this Account: (i) the varia-

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tional minimization of the energy^{16,17,19–33} and (ii) the nonvariational solution of a contracted Schrödinger equation (CSE).^{8–15,34–51} The variational calculation of the 2-RDM constrained by necessary N -representability conditions yields a *lower bound* on the ground-state energy in a given finite basis set. The 2-RDM method yields ground-state energies with useful accuracy even when the wave function becomes difficult to parametrize as in transition-state structures or other stretched geometries of a potential energy surface.^{21,22,27,28,30} Variational solution of the 2-RDM with positivity constraints requires a special constrained optimization known as *semidefinite programming*, which also has applications in control theory, combinatorial optimization, and even finance. In the second approach, the 2-RDM is computed by solving a system of equations known as the contracted Schrödinger equation (CSE).^{8–15,34–51} The CSE is a projection of the N -electron Schrödinger equation onto the space of two electrons. With the 3- and 4-RDMs in the CSE approximated as functionals of the 2-RDM,^{14,15,35,39,40} the CSE is solved self-consistently for the energy and 2-RDM.^{9,10,41,42,50,51}

II. Variational Principle and N -Representability

In quantum mechanics, the ground-state energy of any N -electron atom or molecule with Hamiltonian \hat{H} may be computed in principle from the expectation value of the Hamiltonian with respect to the ground-state wave function $\Psi(1,2,\dots,N)$

$$E = \int \Psi^*(1,2,\dots,N) \hat{H} \Psi(1,2,\dots,N) d1 d2 \dots dN. \quad (3)$$

Because the electrons are indistinguishable with pairwise interactions, the N -electron Hamiltonian in eq 3 may be replaced by an effective two-electron Hamiltonian operator, known as the reduced Hamiltonian operator,

$${}^2\hat{K} = N \left(-\frac{1}{2} \nabla_1^2 - \sum_j \frac{Z_j}{r_{1j}} \right) + \frac{N(N-1)}{2} \frac{1}{r_{12}}. \quad (4)$$

Since the reduced Hamiltonian depends only upon electrons one and two, it may be moved outside the integration over electrons three to N to obtain

$$E = \int^2 \hat{K} \left(\int \Psi(1,2,\dots,N) \Psi^*(1',2',\dots,N) d3 \dots dN \right) d1 d2 \quad (5)$$

or

$$E = \int^2 \hat{K}^2 \mathbf{D}(1,2;1',2') d1 d2, \quad (6)$$

where the inner integration of the wave function over electrons three through N in eq 5 defines the 2-RDM $\mathbf{D}(1,2;1',2')$ ^{3,4} in eq 6. From a knowledge of the 2-RDM, we can compute any two-electron properties of an atom or molecule.

How can we generate N -representability conditions so that we can optimize the ground-state energy variationally as a functional of the 2-RDM? Consider acting on the ground-state wave function with the operators $\{\hat{C}_i\}$ to generate a set of basis functions $\{|\Phi_i\rangle\}$

$$|\Phi_i\rangle = \hat{C}_i |\Psi\rangle. \quad (7)$$

The metric (or overlap) matrix \mathbf{M} associated with these basis functions

$$M_j^i = \langle \Phi_i | \Phi_j \rangle = \langle \Psi | \hat{C}_i^\dagger \hat{C}_j | \Psi \rangle \quad (8)$$

must be positive semidefinite, which we denote as $\mathbf{M} \geq 0$. A matrix is *positive semidefinite* if and only if its eigenvalues are nonnegative. If the elements of the metric matrix may be evaluated only with a knowledge of the p -RDM, then the condition $\mathbf{M} \geq 0$ is a *p -positivity condition*, which restricts the N -representability of the p -RDM.¹⁷

To illustrate the positivity conditions concretely, we begin by considering the 1-positivity conditions whose metric matrices may be evaluated from a knowledge of the 1-RDM only. If we choose for each \hat{C}_j a second-quantized operator \hat{a}_j that kills a particle in the j th orbital, we obtain the one-particle reduced density matrix (1-RDM) whose elements are

$${}^1D_j^i = \langle \Psi | \hat{a}_i^\dagger \hat{a}_j | \Psi \rangle. \quad (9)$$

Similarly, if we select for each \hat{C}_i an operator \hat{a}_i^\dagger that creates a particle in the i th orbital, we obtain the 1-hole reduced density matrix (1-HRDM) whose elements are

$${}^1Q_i^j = \langle \Psi | \hat{a}_j \hat{a}_i^\dagger | \Psi \rangle. \quad (10)$$

Physically, the positivity constraint ${}^1\mathbf{D} \geq 0$ corresponds to ensuring that the probability for finding one electron in any orbital remains nonnegative, while the complementary constraint ${}^1\mathbf{Q} \geq 0$ corresponds to ensuring that the probability for not finding one electron (or finding a hole, which is the absence of a particle) remains nonnegative.

The expectation value of the anticommutation relation for *fermions*

$$\hat{a}_j \hat{a}_i^\dagger + \hat{a}_i^\dagger \hat{a}_j = \delta_j^i \quad (11)$$

yields a linear mapping between the matrix elements of ${}^1\mathbf{D}$ and ${}^1\mathbf{Q}$

$${}^1Q_i^j + {}^1D_j^i = \delta_j^i. \quad (12)$$

From this relation, we perceive that the eigenfunctions (or orbitals) that diagonalize the one-particle RDM also diagonalize the one-hole RDM because the Kronecker δ function is invariant under unitary transformations. Hence, the i th eigenvalue (or occupation number) of the one-hole RDM may be expressed in terms of the i th occupation number of the one-particle RDM, n_i , as $1 - n_i$. The nonnegativity of the occupation numbers, $n_i \geq 0$ and $1 - n_i \geq 0$, from one-positivity conditions implies the Pauli exclusion principle that the occupation numbers of the spin-orbitals must lie between zero and one, that is, $0 \leq n_i \leq 1$. Coleman⁶ first proved in 1963 that the four basic conditions for a fermion density matrix plus the one-positivity conditions are not only necessary but also

sufficient constraints for the ensemble N -representability of the 1-RDM; in other words, every one-electron density matrix that obeys the one-positivity conditions derives from at least one N -electron ensemble density matrix.

We now examine the metric matrices that can be expressed from a knowledge of the 2-RDM only. Constraining these matrices to be positive semidefinite yields the two-positivity conditions.^{17,18,21} The basis functions in eq 7 that produce these 2-RDM metric matrices may be naturally grouped into three orthogonal vector spaces according to the number of creation operators in \hat{C} : (i) $\hat{C} \in \{\hat{a}_i\hat{a}_j\}$, (ii) $\hat{C} \in \{\hat{a}_i^\dagger\hat{a}_i^\dagger\}$, and (iii) $\hat{C} \in \{\hat{a}_i^\dagger\hat{a}_j\}$. The elements of the three metric matrices \mathbf{M} from these groups are given by

$${}^2D_{i,j}^{p,q} = \langle \Psi | \hat{a}_q^\dagger \hat{a}_p^\dagger \hat{a}_i \hat{a}_j | \Psi \rangle \quad (13)$$

$${}^2Q_{i,j}^{p,q} = \langle \Psi | \hat{a}_q \hat{a}_p \hat{a}_i^\dagger \hat{a}_j^\dagger | \Psi \rangle \quad (14)$$

$${}^2G_{i,j}^{p,q} = \langle \Psi | \hat{a}_q^\dagger \hat{a}_p \hat{a}_i^\dagger \hat{a}_j | \Psi \rangle. \quad (15)$$

The constraint ${}^2\mathbf{D} \geq 0$ prevents the probability distribution for finding two particles in two orbitals from being anywhere negative, while the constraint ${}^2\mathbf{Q} \geq 0$ enforces this nonnegativity for two holes. Similarly, the condition ${}^2\mathbf{G} \geq 0$ restricts the probability for finding a particle and a hole in any two spin orbitals from being negative.

These three metric matrices for two-positivity, ${}^2\mathbf{D}$, ${}^2\mathbf{G}$, and ${}^2\mathbf{Q}$, are *linearly* related²¹ by rearranging the creation and annihilation operators according to the anticommutation relations:

$${}^2Q_{i,j}^{p,q}/2 = (\delta_i^p - 2{}^1D_i^p) \wedge \delta_j^q + {}^2D_{i,j}^{p,q}/2 \quad (16)$$

and

$${}^2G_{i,j}^{p,q} = \delta_p^i {}^1D_j^q - {}^2D_{p,j}^{i,q} \quad (17)$$

where the 1-RDM arises from the integration (or contraction in a matrix representation) of the 2-RDM

$${}^1D_i^p = \frac{1}{N-1} \sum_j {}^2D_{i,j}^{p,j}, \quad (18)$$

and the symbol \wedge denotes the antisymmetric tensor product known as the Grassmann wedge product.¹³ With contraction, it may be demonstrated that the two-positivity conditions contain the one-positivity conditions. Unlike the one-positivity conditions for the 1-RDM, the two-positivity conditions are necessary but not sufficient for restricting the 2-RDM to be N -representable. As will be shown in the applications, the two-positivity conditions have proven fairly effective constraints for ground-state calculations of many-electron atoms and molecules at both equilibrium and nonequilibrium geometries.^{21,22,27,28,30}

What are the N -representability conditions not included by the two-positivity conditions? Erdahl and Jin¹⁶ and Mazziotti and Erdahl¹⁷ have shown that the two-positivity conditions may be generalized to p -positivity conditions that arise from the metric matrices that can be expressed from only a knowledge of the p -RDM. At the

level of three-positivity, there are four distinct metric matrices for fermions that correspond to restricting the probability distributions to be nonnegative for three particles ${}^3\mathbf{D} \geq 0$, two particles and one hole ${}^3\mathbf{E} \geq 0$, one particle and two holes ${}^3\mathbf{F} \geq 0$, and three holes ${}^3\mathbf{Q} \geq 0$.^{17,21} Full three-positivity conditions have not yet been applied to atoms and molecules, but calculations on spin systems show that the accuracy of the energy and properties converges rapidly with the level of p -positivity with three-positivity yielding excellent results at all interaction strengths even where traditional wave function methods fail.^{17,31} Two different types of partial three-positivity conditions have been proposed: (i) the lifting conditions^{21,31} and (ii) the T_1 and T_2 conditions.^{24,32,52} The latter conditions correspond to the following restrictions: $T_1 = {}^3\mathbf{D} + {}^3\mathbf{Q} \geq 0$ and $T_2 = {}^3\mathbf{E} + {}^3\mathbf{F} \geq 0$. Originally proposed by Erdahl,⁵² the T_1 and T_2 conditions have been applied by Zhao et al.²⁴ to compute the ground states of atoms and molecules at equilibrium geometries with similar or better accuracy than many standard wave function methods. The author has applied a spin- and symmetry-adapted version of the T_2 condition to molecules with similar accuracy at both equilibrium and stretched geometries in nonminimal basis sets.³²

The p -positivity conditions guarantee the nonnegativity of important probability distributions involving different mixtures of particles and holes. Their strength, however, may be further appreciated from their enforcement of important classes of the *generalized uncertainty relations*.¹⁷ Mazziotti and Erdahl have shown that the $2p$ -positivity conditions enforce the generalized uncertainty relations for all pairs of Hermitian p -body operators \hat{C}_1 and \hat{C}_2 , that is,

$$\sigma(\hat{C}_1)\sigma(\hat{C}_2) \geq \frac{1}{2}|\langle \Psi | [\hat{C}_1, \hat{C}_2] | \Psi \rangle| \quad (19)$$

where

$$\sigma(\hat{C}) = \langle \Psi | (\hat{C} - \langle \Psi | \hat{C} | \Psi \rangle)^2 | \Psi \rangle^{1/2}, \quad (20)$$

and the expectation values may be evaluated with the $2p$ -RDMs. Therefore, the two-positivity conditions imply the uncertainty relations for all pairs of one-body operators.

Unlike the optimization of a trial wave function that produces an upper bound on the ground-state energy by the Rayleigh–Ritz variational principle, the variational 2-RDM method with necessary N -representability constraints such as the positivity conditions yields a lower bound on the ground-state energy. For this reason, the variational 2-RDM method has also been called the lower bound method in the literature.¹⁶ The lower bound on the energy, however, is only a signature for a more fundamental difference between the wave function and 2-RDM approaches to many-electron correlation. All wave function methods, whether variational or not, depend on a parametrization of the N -electron wave function. In the variational case, this parametrization leads to the energy upper bound of the Rayleigh–Ritz variational principle, while in nonvariational methods it generates accuracy

through a certain order of perturbation theory. In the variational 2-RDM method, however, the set of 2-RDMs contains all N -representable 2-RDMs, and hence, all wave functions, whether single- or multireferenced, are correctly parametrized. In fact, because the set of 2-RDMs defined by necessary positivity conditions is larger than the set of N -representable 2-RDMs, the 2-RDM is slightly “over-parametrized”, which leads to the lower bounds to the energies of N -electron atoms and molecules. Nevertheless, because the positivity conditions do not depend on a specific reference configuration like the Slater determinant for a single-reference wave function technique, the variational 2-RDM method can treat both single- and multi-reference correlation effects with consistent accuracy. As we will show in the applications, this is especially useful for describing the shape of potential energy surfaces.

III. Semidefinite Programming

Variational calculation of the energy with respect to the 2-RDM constrained by two-positivity conditions requires minimizing the energy in eq 5 while restricting the ${}^2\mathbf{D}$, ${}^2\mathbf{Q}$, and ${}^2\mathbf{G}$ to be not only positive semidefinite but also interrelated by the linear mappings in eqs 16–18. This is a special optimization problem known as a *semidefinite program*. The solution of a semidefinite program is known as *semidefinite programming*.

In the mid-1990s, a powerful family of algorithms, known as *primal-dual interior-point algorithms*, were developed for solving semidefinite programs.⁵³ The phrase *interior-point* means that the method keeps the trial primal and dual solutions on the *interior* of the feasible set throughout the solution process. In these algorithms, a good initial guess for the 2-RDM is a scalar multiple of the two-particle identity matrix. Advantages of the interior-point methods are (i) rapid quadratic convergence from the identity matrix to the optimal 2-RDM for a set of positivity conditions and (ii) a rigorous criterion in the duality gap for convergence to the global minimum. These benefits, however, come with large memory requirements and a significant number of floating-point operations per iteration, specifically $O(nm^3 + n^2m^2)$ where n is the number of variables and m is the number of constraints. With m and n proportional to the number of elements in the 2-RDM ($\sim r^4$), the method scales approximately as r^{16} where r is the rank of the one-particle basis set.^{21,23} The variational 2-RDM method has been explored for minimal basis sets with the primal-dual interior-point algorithm, but the computational scaling significantly limits both the number of active electrons and the size of the basis set.^{20–24,26}

The author has recently developed a large-scale semidefinite programming algorithm for solving the semidefinite program in the variational 2-RDM method.^{27,28} The optimization challenge in the 2-RDM method is to constrain the metric matrices to be positive semidefinite while the ground-state energy is minimized. The algorithm constrains the solution matrix \mathbf{M} to be positive semidefinite by a matrix factorization

$$\mathbf{M} = \mathbf{R}\mathbf{R}^*, \quad (21)$$

where for the two-positivity conditions

$$\mathbf{M} = \begin{pmatrix} {}^2\mathbf{D} & 0 & 0 \\ 0 & {}^2\mathbf{Q} & 0 \\ 0 & 0 & {}^2\mathbf{G} \end{pmatrix}. \quad (22)$$

Such a matrix factorization was previously considered in the context of 2-RDM theory by Rosina,⁵⁴ Harriman,⁵⁵ and the author,¹³ and it was recently employed for solving large-scale semidefinite programs in combinatorial optimization.⁵⁶ The linear constraints, including the trace, the contraction, and the interrelations between the metric matrices, become quadratic in the new independent variables \mathbf{R} . Therefore, the factorization in eq 21 converts the semidefinite program into a *nonlinear program* where the energy must be minimized with respect to \mathbf{R} while nonlinear constraint equalities are enforced.

We solve the nonlinear formulation of the semidefinite program by the augmented Lagrange multiplier method for constrained nonlinear optimization.^{27,28} Consider the augmented Lagrangian function

$$L(\mathbf{R}) = E(\mathbf{R}) - \sum_i \lambda_i c_i(\mathbf{R}) + \frac{1}{2\mu} \sum_i c_i(\mathbf{R})^2, \quad (23)$$

where \mathbf{R} is the matrix factor for the solution matrix \mathbf{M} , $E(\mathbf{R})$ is the ground-state energy as a function of \mathbf{R} , $\{c_i(\mathbf{R})\}$ is the set of equality constraints, $\{\lambda_i\}$ is the set of Lagrange multipliers, and μ is the penalty parameter. For an appropriate set of multipliers $\{\lambda_i\}$, the minimum of the Lagrangian function with respect to \mathbf{R} corresponds to the minimum of the energy $E(\mathbf{R})$ subject to the nonlinear constraints $c_i(\mathbf{R})$. The positive third term in the augmented Lagrangian function, known as the quadratic penalty function, tends to zero as the constraints are satisfied. Evaluating the function and its gradient costs approximately r^6 floating-point operation,²⁷ mainly from the matrix multiplication of the block-diagonal \mathbf{R} matrix with itself, where r is the rank of the one-particle basis set. Storing the factorized 2-RDM, several copies of its gradient, and the Lagrange multipliers scales as r^4 . In comparison with the primal-dual interior-point approach, which scales as r^{16} and r^8 in floating-point operations and memory storage, the first-order nonlinear algorithm for the variational 2-RDM method^{27,28} offers a significant improvement in computational efficiency.

IV. Contracted Schrödinger Equation

The N -particle Schrödinger equation may be integrated (or contracted) onto the space of two particles to obtain a contracted Schrödinger equation^{8–15,34–51}

$$\int \hat{H}\Psi(1,2,\dots,N)\Psi^*(1',2',\dots,N') d3 d4 \dots dN = E^2 D(1,2;1',2'). \quad (24)$$

Because the Hamiltonian contains only pairwise interactions, the left-hand side of the CSE can be expressed

directly in terms of the 2-, 3-, and 4-RDMs without the many-electron wave function.

Valdemoro and co-workers⁸ realized in 1993 that the 2-RDM might be directly computed with the CSE if the 3- and 4-RDMs were approximated as functionals of the 2-RDM. In 1994 Colmenero and Valdemoro⁹ presented preliminary results for atoms and molecules, in 1996 Nakatsuji and Yasuda^{10,11} solved the CSE with Green's function approximations for the 3- and 4-RDMs, and in 1998 the author systematized the reconstruction of the 3- and 4-RDMs by using cumulant theory for RDMs.^{13–15,35,37–39} The cumulant expansion of the 3-RDM in terms of the lower RDMs may be written as

$${}^3\mathbf{D}/6 = {}^1\mathbf{D}\wedge{}^1\mathbf{D}\wedge{}^1\mathbf{D} + 3 {}^2\Delta\wedge{}^1\mathbf{D} + {}^3\Delta, \quad (25)$$

where

$${}^2\Delta = {}^2\mathbf{D}/2 - {}^1\mathbf{D}\wedge{}^1\mathbf{D}, \quad (26)$$

and the symbol \wedge denotes the antisymmetric tensor product or Grassmann wedge product.¹³ The term ${}^3\Delta$ is the cumulant or connected part of the 3-RDM that cannot be written as a sum of wedge products involving the lower RDMs. A similar cumulant expansion for the 4-RDM may be given in terms of the 1-RDM and the cumulant parts of the 2-, 3-, and 4-RDMs. At the simplest level of approximation the 3- and 4-RDMs may be reconstructed from the 2-RDM by neglecting their cumulant parts.

The reconstruction of the higher RDMs from the 2-RDM is justified by Rosina's theorem.¹³ For any system with just pairwise interactions, as long as the ground state is nondegenerate, there is a one-to-one mapping between the ground-state 2-RDM and its N -electron wave function. Rosina originally made this observation in 1967, and the author reintroduced his idea as a theorem in 1998.¹³ The short proof is as follows. Assume that there are two wave functions, Ψ_1 and Ψ_2 , that contract to the same 2-RDM. Since the energy may be evaluated from the 2-RDM by eq 3, both wave functions have the same energy. By the Rayleigh–Ritz variational principle, however, there are two ground-state wave functions, Ψ_1 and Ψ_2 , with the same energy, which contradicts the assumption that the ground-state wave function is nondegenerate. As a corollary, the ground-state 2-RDM uniquely determines all of the higher p -RDMs for $p > 2$.¹³ Unlike the one-density functionals, these reconstructions (or universal functionals of the ground-state 2-RDM) are valid or universal for any type of two-particle interaction.

With reconstruction the CSE may be iteratively solved for an approximation to the correlated 2-RDM. Initial applications were made to atoms and molecules by Colmenero and Valdemoro^{9,12} and Nakatsuji and Yasuda^{10,11} and to the Lipkin spin model by Mazziotti.^{13–15,39} For the Lipkin model, the CSE yields ground-state energies and 2-RDMs that are more accurate than either second- or fourth-order many-body perturbation theory and similar in accuracy to the coupled-cluster singles-doubles method.³⁹ Contrary to the findings of Harris,⁴³ computational experience shows clearly that in

the Lipkin model using either the Nakatsuji–Yasuda or the Mazziotti correction to the 3-RDM is critical to convergence as well as accuracy.^{13,39}

To solve the CSE iteratively for atoms and molecules, the author found it necessary to correct the positivity of the two-particle and two-hole RDMs, respectively.^{41,42} By analogy with the purification methods employed in linear-scaling 1-RDM calculations, these methods for correcting the 2-RDM's N -representability were given the name correlated purification.⁴¹ The poor results from Nooijen and co-workers⁴⁵ follow from solving the CSE without any correlated purification to enforce N -representability. The author's calculations demonstrate that by using reconstruction and purification the CSE may be solved for atoms and molecules with an accuracy that is better than second-order many-body perturbation theory although not presently as accurate as the coupled-cluster singles-doubles method.^{41,42} Alcoba and Valdemoro⁵⁰ have recently developed a new correlated purification strategy that includes correction of ${}^2\mathbf{G} \geq 0$. Their calculations with the CSE exhibit convergence and accuracy similar to that reported by the author.⁵¹

V. Applications of the 2-RDM

The variational 2-RDM method has been applied to a variety of atoms and molecules at both equilibrium and stretched geometries. We will summarize calculations on a variety of molecules: (i) the nitrogen molecule,³⁰ (ii) a set of organic molecules,²⁹ (iii) a set of inorganic molecules,³² (iv) the hydroxide radical,³³ and (v) a hydrogen chain.²⁷ Finally, we illustrate the self-consistent solution of the CSE in a calculation on water.⁴¹

A challenging correlation problem is the accurate description of the stretching and dissociation of the triple bond in nitrogen. Six-to-eight-particle excitations from the Hartree–Fock determinant are required to treat the nitrogen dissociation correctly. Using a correlation-consistent polarized double- ζ basis set, we compare in Figure 1a,b the shape of the potential curve for nitrogen from the variational 2-RDM method with the curves from several wave function methods including full configuration interaction (FCI).³⁰ The 2-RDM energies are consistent lower bounds to the FCI energies throughout the stretch. In the figure, we present the 2-RDM curve shifted by the difference between the 2-RDM and CCSD(T) energies at equilibrium. The 2-RDM method yields a potential energy curve that is more accurate than the single-reference methods in Figure 1a and equally accurate as the multi-reference methods in Figure 1b. The equilibrium bond distance and the harmonic frequency from the 2-RDM method are 1.1167 Å and 2311 cm⁻¹ (Table 1), which is in good agreement with the FCI numbers, 1.1172 Å and 2321 cm⁻¹. Multireference configuration interaction with single-double excitations yields 1.1184 Å and 2311 cm⁻¹.

The 2-RDM method has been applied to a large set of organic molecules²⁹ to examine trends with functional groups. Table 2 shows a set of organic molecules computed by the 2-RDM method in an STO-6G basis set to

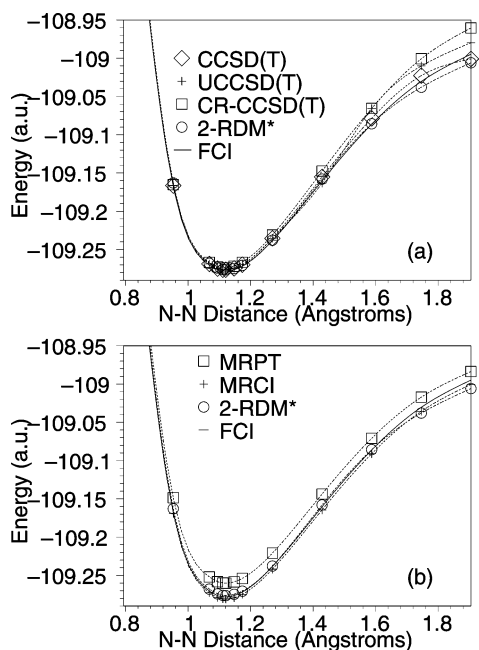


FIGURE 1. The shape of the potential curve for nitrogen in a correlation-consistent polarized double- ζ basis set for the variational 2-RDM method, as well as (a) single-reference coupled cluster, (b) multireference second-order perturbation theory (MRPT) and single-double configuration interaction (MRCI), and full configuration interaction (FCI) wave function methods. The symbol 2-RDM* indicates that the potential curve was shifted by the difference between the 2-RDM and CCSD(T) energies at equilibrium.

Table 1. The Equilibrium Bond Distance and the Harmonic Frequency for N_2 from the 2-RDM Method with Two-Positivity (DQG) Conditions Compared with Their Values from Coupled-Cluster Singles-Doubles with Perturbative Triples (CCSD(T)), Multireference Second-Order Perturbation Theory (MRPT), Multireference Configuration Interaction with Single-Double Excitations (MRCI), and Full Configuration Interaction (FCI)^a

method	R_{eq} (Å)	ω (cm^{-1})
CCSD(T)	1.1185	2344
MRPT	1.1176	2309
MRCI	1.1184	2311
2-RDM	1.1167	2311
FCI	1.1172	2321

^a All methods employ a correlation-consistent polarized double- ζ basis set.

illustrate trends with (i) molecular size, (ii) hybridization, (iii) electronegativity, and (iv) atomic radius. The first six rows of the table show the alkane chains from methane through hexane. The 2-RDM method is *size extensive*, that is, the error in its energy remains constant with increasing molecular size. Comparing the errors in the percentage of the correlation for propane, 1-propene, and 1-propyne reveals that the error is greater when the atoms have more p character in their hybridization. Third, if a hydrogen is replaced with a more electronegative functional group like OH, the accuracy of the 2-RDM increases, as seen in the comparison of propane and propanol, and if an oxygen atom is replaced with an atom of larger size such as sulfur, the 2-RDM accuracy decreases, as seen in the comparison of propanol and propanthiol. These trends reflect the

Table 2. Accuracy of Variational RDM Theory Subject to Two-Positivity for a Set of Organic Molecules^a

molecule	CCSD(T)		error in % of correlation energy	
	E_{ground}^c	E_{corrln}^d	no correction	correction
methane	-40.191	-0.082	+24.8	-3.8
ethane ^b	-79.261	-0.153	+29.8	+0.0
propane	-118.241	-0.224	+32.0	+1.7
butane	-157.268	-0.296	+33.3	+2.8
pentane	-196.294	-0.368	+33.8	+3.1
hexane	-235.321	-0.440	+32.6	+2.2
1-propene	-117.023	-0.239	+30.5	+1.6
1-propyne	-115.810	-0.244	+26.1	+0.8
propanol	-192.823	-0.275	+30.3	+2.3
2-propanone ^b	-191.663	-0.296	+29.1	+0.0
1-propanal	-191.654	-0.298	+28.7	+1.5
2-propynal	-189.222	-0.320	+24.6	+0.9
2-methyl-2-propenal	-229.470	-0.384	+29.7	+2.2
propanoic acid	-266.266	-0.348	+26.8	+0.2
propylamine	-173.140	-0.291	+31.6	+1.1
propanamide	-246.576	-0.359	+28.9	+0.5
propanethiol	-514.435	-0.220	+50.9	+4.2
methyl-cyclopropane	-156.040	-0.292	+35.2	+2.0
cyclopropylamine	-171.923	-0.287	+34.1	+1.0
cyclopropanone	-190.415	-0.296	+32.0	+0.3
cyclopropanol	-191.598	-0.270	+33.1	+2.9
methyl cyclopropyl ether	-230.629	-0.343	+34.5	+2.1
cyclopropionic acid	-304.074	-0.414	+30.1	+1.1
cyclopropane thiol	-513.210	-0.220	+52.6	+0.1

^a Total energies and correlation energies are reported in hartrees (hartree). All values reported are calculated at the CCSD(T) equilibrium geometry. ^b Indicates a molecule used to calibrate the functional-group correction scheme. ^c Ground-state energy. ^d Correlation energy.

Table 3. For Three Molecules in Valence Double- ζ Basis Sets, Comparison of Energies in hartrees (hartree) from the 2-RDM Method with the T_2 Condition (DQGT2) with the Energies from Second-Order Many-Body Perturbation Theory (MP2), Coupled Cluster Method with Single-Double Excitations and a Perturbative Triples Correction (CCSD(T)), and Full Configuration Interaction (FCI)

molecule	total FCI energy	error in (mhartree)		
		MP2	CCSD(T)	DQGT2
CH ₂	-38.9465	+23.3	+0.6	-0.1
BeH ₂	-15.8002	+11.8	+0.2	-0.2
H ₂ O	-76.1411	+8.0	+0.5	-1.8

systematic nature of the positivity conditions and suggest a straightforward correction to the 2-RDM energies for organic molecules based on functional groups.²⁹ With the functional group correction, the 2-RDM predicts the ground-state energies for a wide range of organic molecules within a few percent of the total correlation energy.

The N -representability conditions on the 2-RDM can be systematically strengthened by adding some of the three-positivity constraints to the two-positivity conditions. For three molecules in valence double- ζ basis sets, Table 3 shows that the 2-RDM method with the T_2 condition (DQGT2) yields energies at equilibrium geometries that are similar in accuracy to the coupled cluster method with single-double excitations and a perturbative triples correction. The error is reported in millihartrees (mhartree).

Computation of open-shell molecular energies and properties is important in many areas of chemistry from

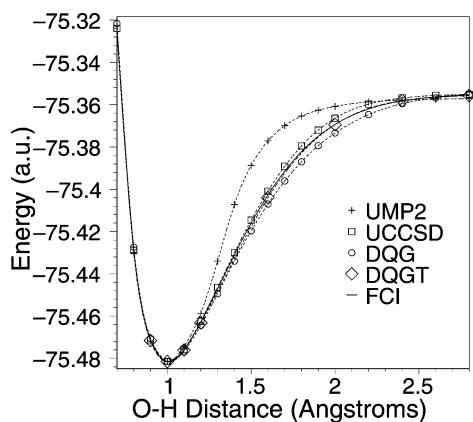


FIGURE 2. The shapes of the potential energy curves of the OH radical from the 2-RDM methods with DQG and DQGT2 conditions, as well as the approximate wave function methods UMP2 and UCCSD, compared with the shape of the FCI curve. The potential energy curves of the approximate methods are shifted by a constant to make them agree with the FCI curve at equilibrium or 1.00 Å. The 2-RDM method with the DQGT2 conditions yields a potential curve that within the graph is indistinguishable in its contour from the FCI curve.

combustion and atmospheric chemistry to medicine, yet such molecules are often challenging due to the appearance of multireference spin effects. We have recently extended the variational 2-RDM method from closed-shell to open-shell molecules.³¹ The *shape* of the potential energy curve of the OH radical is shown in Figure 2 from the 2-RDM methods with two-positivity (DQG) and two-positivity plus T_2 (DQGT2) conditions as well as the wave function methods unrestricted second-order many-body perturbation theory (MBPT2), unrestricted coupled-cluster singles-doubles (UCCSD), and full configuration interaction (FCI). The potential energy curves of the approximate methods have been shifted by a constant to make them agree with the FCI curve at equilibrium. In the bonding region, the 2-RDM/DQG, UCCSD, and FCI curves are nearly indistinguishable whereas in the stretched-bond region the 2-RDM/DQG and UCCSD curves move away slightly from the FCI solution in opposite directions. Recently, we have implemented a spin- and symmetry-adapted form of the T_2 constraint within the large-scale semidefinite-programming algorithm for the 2-RDM method.³² For OH, the 2-RDM method with the DQGT2 conditions yields potential curves whose shapes in the figures are indistinguishable from the shapes of the FCI curves.

Metallic hydrogen is an infinite chain of equally spaced hydrogen atoms. It can serve as a simple model for polymers and crystals. We consider the equally spaced, finite chain H_6 where the hydrogen atoms are described by the valence triple- ζ basis set. A potential energy curve may be formed by equally stretching the five bonds in H_6 . Ground-state energies from the variational 2-RDM method and a variety of wave function techniques are shown in Figure 3 as functions of the distance R between adjacent hydrogen atoms.²⁷ The 2-RDM method yields consistent energies with a maximum error of -10.8 mhartree at 1.5

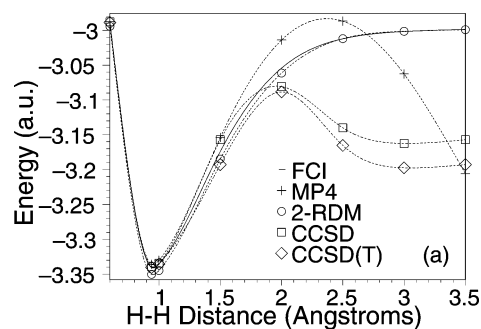


FIGURE 3. Ground-state potential energy curves of H_6 from 2-RDM and wave function methods. MP2 and MP4 denote second- and fourth-order perturbation theories, while CCSD and CCSD(T) represent coupled cluster methods.

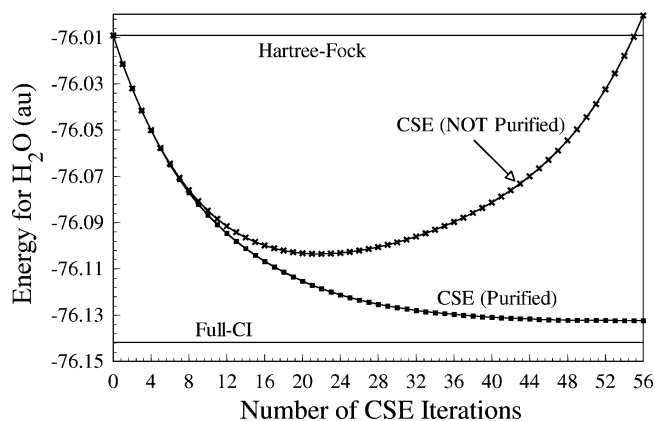


FIGURE 4. The ground-state electronic energy for H_2O is shown as a function of the CSE iterations both with and without purification. The CSE with purification captures 92.8% of the correlation energy, but the CSE without purification achieves only 71.2% of the correlation energy before diverging.

Å. While the coupled cluster methods are accurate near the equilibrium geometry with errors at 1 Å of 1.3 mhartree (CCSD) and 0.2 mhartree (CCSD(T)), their performance rapidly degrades as the bonds are stretched. At 3.5 Å, each of the coupled cluster methods has an energy error of at least -160 mhartree, while the 2-RDM method has an error of only -0.4 mhartree.

The nonvariational calculation of the 2-RDM by the iterative solution of the CSE for the water molecule in a double- ζ basis set is shown in Figure 4.^{21,23} The ground-state electronic energy for H_2O is given 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.²³ The contracted power method with purification^{21,23} overcomes convergence problems reported by Nakatsuji and Yasuda^{11,34} to yield consistent movement toward the N -particle solution at each CSE iteration. Because the CSE implicitly depends on a Slater reference through its cumulant expansion, it does not capture multireference effects along a bond stretch as accurately as the variational 2-RDM method.

VI. A Look Ahead

Since the time that Coulson⁷ discussed the promise and challenges of computing the energies and properties of atoms and molecules without the many-electron wave function, quantum chemistry has experienced many important advances toward the accurate treatment of electron correlation including the development of density functional theory, coupled cluster theory, Monte Carlo methods, and multireference perturbation theory. The recent progress in the 2-RDM methods contributes both a new perspective and tool for describing energies and properties of atoms and molecules in which correlation effects are accounted. As has been discussed, two different complementary methods for the direct calculation of the 2-RDM have been developed: (i) the variational calculation with the constraint of the 2-RDM by N -representability conditions^{16,17,20–33} and (ii) the solution of the contracted Schrödinger equation with the 2-RDM constrained by the structure of the CSE, as well as N -representability conditions.^{8–15,34–51} Unlike the variational wave function techniques, the variational 2-RDM method yields lower bounds on the ground-state energy in a given basis set; the CSE yields nonvariational energies. The variational 2-RDM is especially applicable to treat molecular systems with difficult-to-parametrize wave functions that arise in chemistry at transition states and other nonequilibrium geometries, as well as in describing many open-shell molecules.

With the foundations of 2-RDM theory established, there remain many open challenges and possibilities. In the variational method greater experience with the positivity conditions and developments in large-scale algorithms for semidefinite programming²⁷ are expected to improve further both their accuracy and their efficiency, and in the nonvariational CSE methods improvements in correlated purification,^{23,50} reconstruction of the higher RDMs,^{14,35,39} and other areas will likewise enhance performance. The 2-RDM methods may be especially well-suited for the use of explicitly correlated basis sets for enhancing basis set convergence. The calculation of the 2-RDM has important applications in chemistry to studying reactivity^{29,30} as well as in other areas of correlation such as spin systems like the Hubbard model, Bose condensation,²⁵ and molecular conductivity. While still in its early stages, the 2-RDM method for computing energies and properties without the many-electron wave function represents a new approach to investigating the electronic structure of atomic and molecular systems.

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