Pure-N-representability conditions of two-fermion reduced density matrices

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Pure N-representability Conditions of Two-Fermion Reduced Density Matrices

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We derive necessary conditions for any 2-fermion reduced density matrix (2-RDM) to be representable by a pure N-fermion density matrix $\Psi\Psi^*$ where Ψ is the wave function. These pure N-representability conditions of the 2-RDM are important because they provide stringent constraints beyond those from the Pauli and the generalized Pauli constraints on the structure of many-fermion 2-RDMs and their wave functions. The pure 2-RDM conditions are derived as generalized Pauli constraints on effective one-fermion reduced density matrices (1-RDMs) generated by the removal or addition of a fermion from the wave function. Computationally, we show for 4-electron molecules that the derived pure N-representability conditions are non-trivially active for exact ground-state 2-RDMs and that they provide significant restrictions beyond the D, Q, and G ensemble N-representability conditions. Constraints on higher-order p-RDMs where $p > 2$ are derived in a similar fashion. The constraints have potentially significant applications to computing strongly correlated many-fermion states with enhanced accuracy and decreased computational complexity.

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I. INTRODUCTION

In 1925 Pauli [1] recognized that for fermions the occupation of a spin orbital must lie between zero and one. The following year Heisenberg [2] and Dirac [3] recognized that the Pauli exclusion principle can be generalized by requiring that the many-fermion wave function be antisymmetric in the exchange of the spin spatial coordinates for a pair of fermions. In 1963 Coleman [4–6] proved that the Pauli constraints on the one-fermion reduced density matrix (1-RDM), which require its eigenvalues to lie between 0 and 1, are necessary and sufficient conditions for its integration from at least one N-electron ensemble density matrix, known as *ensemble N-representability conditions*. The scenario, originally considered by Heisenberg and Dirac, that the 1-RDM is representable by an N-fermion wave function, or more precisely derivable from an N-fermion pure density matrix $\Psi\Psi^*$, implies additional restrictions on the 1-RDM beyond the Pauli constraints, known as *pure N-representability conditions* or *generalized Pauli constraints* [4, 7–25]. In 2008 Altunbulak and Klyachko [10, 11] employed enumerative geometry in the form of Schubert calculus to derive the generalized Pauli constraints on the 1-RDM, which have recently been explored numerically for the ground and excited states of harmonic and spin systems [12, 18, 19, 23], few-electron atoms and molecules [13–15, 20, 21, 24, 25], as well as time-dependent and open quantum systems [16]. Remarkably, these calculations have shown that for many 3-electron systems the ground-state wave functions have 1-RDMs whose eigenvalue spectra are pinned to the generalized Pauli constraints. An eigenvalue spectra is said to be *pinned* (or quasi-pinned) to an inequality constraint if it saturates (or nearly saturates) the inequality. This pinning implies a simplification of the structure of the many-electron wave function [12, 14, 24, 25] with implications for the treatment of strongly correlated quantum systems.

While mathematical constructions of the generalized Pauli constraints on the 1-RDM [10, 11] and the ensemble N-representability constraints on the 2-fermion reduced density matrix (2-RDM) [26–29] are known, not much is known about the pure N-representability of the 2-RDM [6, 9, 11]. In this paper we derive a large set of necessary pure N-representability conditions on the 2-RDM and higher p-RDMs that extends the generalized Pauli constraints on the 1-RDM to the 2- and higher-fermion RDMs. The key insight is that the ionization of a pure N-fermion quantum system generates a pure $(N-1)$-fermion quantum system whose 1-RDM must also satisfy the generalized Pauli constraints. Because the 1-RDM of the ionized quantum system is expressible in terms of the 2-RDM of the N-fermion quantum system, the 1-RDM's generalized Pauli constraints generate pure N-representability constraints on the 2-RDM. By *particle-hole symmetry* additional pure constraints on the 2-RDM are derivable from the attachment of a fermion to the N-fermion quantum system. In addition to being previously unknown, pure N-representability conditions on the 2-RDM are important because the pinning of the 2-RDM to these conditions enforces special structure on the class of ground-state 2-RDMs and many-fermion wave functions, which potentially can be exploited to decrease the computational scaling of strongly correlated many-fermion systems, i.e. through the exploitation of implied sparsity in the expansion of the wave function [12, 25] or implied restrictions on the feasible set of 2-RDMs in variational 2-RDM calculations [6, 30–52].

Computationally, the pure N-representability conditions derived for arbitrary N are explored on several four-electron molecules including H_4, HeH^-, He_2, BeB^+, and

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Be$_2$. First, we show that the ground-state wave function of each of these molecules is pinned to the boundary of the necessary conditions. This observation is important because it demonstrates (*i*) that the boundary of the approximate set of 2-RDMs generated by the necessary conditions touches the boundary of the exact pure N-representable set of 2-RDMs and (*ii*) that the special structure implied by pinning to the conditions is *not* an approximation for these molecules' wave functions and 2-RDMs. Second, we show that combining the pure conditions with the typically employed ensemble N-representability conditions, the D, Q, and G conditions [6], is more stringent than the ensemble conditions alone. Specifically, the approximate 2-RDMs from variational minimization with respect to the D, Q, and G conditions alone are shown to violate these pure N-representability conditions.

TABLE I. A 1-RDM is pure 3-representable by a 3-fermion wave function in 7 orbitals if and only if the four one-fermion operators, given in this table in the eigenfunction (diagonal) basis of the 1-RDM, have non-negative expectation values [11].

$$^1\hat{O}_1 = 2 - \hat{a}_2^\dagger\hat{a}_2 - \hat{a}_3^\dagger\hat{a}_3 - \hat{a}_4^\dagger\hat{a}_4 - \hat{a}_5^\dagger\hat{a}_5$$

$$^1\hat{O}_2 = 2 - \hat{a}_1^\dagger\hat{a}_1 - \hat{a}_3^\dagger\hat{a}_3 - \hat{a}_4^\dagger\hat{a}_4 - \hat{a}_6^\dagger\hat{a}_6$$

$$^1\hat{O}_3 = 2 - \hat{a}_1^\dagger\hat{a}_1 - \hat{a}_2^\dagger\hat{a}_2 - \hat{a}_4^\dagger\hat{a}_4 - \hat{a}_7^\dagger\hat{a}_7$$

$$^1\hat{O}_4 = 2 - \hat{a}_1^\dagger\hat{a}_1 - \hat{a}_2^\dagger\hat{a}_2 - \hat{a}_5^\dagger\hat{a}_5 - \hat{a}_6^\dagger\hat{a}_6$$

II. THEORY

The pure N-representability conditions of the 1-RDM, or the generalized Pauli constraints, can be expressed in terms of the eigenvalues of the 1-RDM [4, 7–25]. Working at IBM in 1972, Borland and Dennis [8] discovered the following constraints on three-electron systems in six orbitals:

$$\lambda_5 + \lambda_6 - \lambda_4 \geq 0 \tag{1}$$

$$\lambda_1 + \lambda_6 = 1 \tag{2}$$

$$\lambda_2 + \lambda_5 = 1 \tag{3}$$

$$\lambda_3 + \lambda_4 = 1 \tag{4}$$

where the eigenvalues λ_i are ordered from largest to smallest. These additional conditions beyond the Pauli constraints are necessary for the 1-RDM to be representable by an N-electron wave function. Generalization of the Borland-Dennis constraint to larger numbers of particles and orbitals, derived by Altunbulak and Klyachko [10, 11], provides a hierarchy of necessary and sufficient conditions that characterize set of pure N-representable 1-RDMs.

The set $P^1_{N,r}$ of pure N-representable 1-RDMs in r orbitals is expressible in general as

$$\{^1D|\mathrm{Tr}(^1\hat{O}_m\ ^1D) \geq 0\ \forall ^1\hat{O}_m \in B^1_{N,r}\} \tag{5}$$

where $B^1_{N,r}$ is the set of operators that expose the boundary of $P^1_{N,r}$. An operator is said to *expose* a convex set if its expectation value over points in the set has its minimum at a point (or points) on the boundary. In the present case each operator in $B^1_{N,r}$ has a nonnegative expectation value for each point inside the set $P^1_{N,r}$ with a minimum expectation value of zero at a point (or points) on the boundary of $P^1_{N,r}$. Because the N-representability of RDMs is invariant under unitary transformations of the orbital basis set, the N-representability of the 1-RDM depends only upon its eigenvalues [4]. Consequently, without approximation we can restrict the set $P^1_{N,r}$ to 1-RDMs in a given eigenfunction (diagonal) basis set with eigenvalues ordered in a non-increasing sequence. In this case the set $P^1_{N,r}$ becomes a convex polytope with diagonal operators $^1\hat{O}_m$ defining its facets. For example, for three electrons in seven orbitals there exist four distinct operators $^1\hat{O}_m$, given in Table I where $\hat{a}_i^\dagger$ and $\hat{a}_i$ are the creation and annihilation operators with respect to orbital i [11]. In Table I, if the second-quantized operators associated with the seventh natural orbital are neglected, then the operators $^1\hat{O}_m$, define a set of inequalities that can be shown to be equivalent to the Borland-Dennis constraints in Eqs. (1-4).

Necessary pure N-representability conditions on the 2-RDM can be derived by applying the generalized Pauli constraints to a parameterized family of effective 1-RDMs. They are presented in the following theorem:
Theorem: If a 2-RDM is pure N-representable by a wave function Ψ in the space $\wedge^N_r H$, then it must satisfy the following constraints:

$$\mathrm{Tr}(^1\hat{O}_m\ ^1\tilde{D}) \geq 0 \quad \forall ^1\hat{O}_m \in B^1_{N-1,r-1} \tag{6}$$

in which

$$^1\tilde{D}^q_t = \kappa \sum_{p,s} c^*_p\ ^2D^{pq}_{st}\ c_s. \tag{7}$$

where the effective 1-RDM $^1\tilde{D}$ is expressible in terms of the 2-RDM, the arbitrary parameters c_s, and the constant κ that normalizes $^1\tilde{D}$ to $(N-1)$ and the indices p, q, s, and t, ranging from 1 to r, denote the orbitals. *Proof*: Consider the evaluation of the generalized Pauli constraints

$$\langle\tilde{\Psi}|^1\hat{O}_m|\tilde{\Psi}\rangle \geq 0 \quad \forall ^1\hat{O}_m \in B^1_{N-1,r-1} \tag{8}$$

where $\tilde{\Psi}$ is an $(N-1)$-fermion wave function generated by removing a particle from the N-fermion wave function

$$|\tilde{\Psi}\rangle = \left(\sum_s c_s\hat{a}_s\right)|\Psi\rangle \tag{9}$$

$$|\tilde{\Psi}\rangle = \hat{a}_u|\Psi\rangle \tag{10}$$

in which $|\phi_u\rangle = \sum_s c_s|\phi_s\rangle$. Eq. (10) shows that not only a fermion but also the transformed orbital $|\phi_u\rangle$ is removed, and hence, $\tilde{\Psi}$ lies in the space $\wedge_{r-1}^{N-1}H$. The choice of the parameters c_s determines the orbital $|\phi_u\rangle$ that is removed. Substituting Eq. (9) into Eq. (8) and using the second-quantized expansion of the ${}^1\hat{O}_m$ operators

$$ {}^1\hat{O}_m = \sum_{qt} ({}^1\hat{O}_m)^q_t \hat{a}^\dagger_q \hat{a}_t, \tag{11} $$

we obtain

$$ \kappa \sum_{qt} ({}^1\hat{O}_m)^q_t \sum_{ps} c^*_p \langle\Psi|\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_t \hat{a}_s|\Psi\rangle c_s \geq 0 \tag{12} $$

$$ \kappa \sum_{qt} ({}^1\hat{O}_m)^q_t \sum_{ps} c^*_p \, {}^2D^{pq}_{st} \, c_s \geq 0 \tag{13} $$

$$ \sum_{qt} ({}^1\hat{O}_m)^q_t \, {}^1\tilde{D}^q_t \geq 0, \tag{14} $$

with Eq. (14) being equivalent to Eq. (6).

Physically, the pure N-representable 2-RDM conditions in the theorem can be understood in terms of electron detachment or ionization. The ground states of many three-electron quantum systems have been shown to be pinned to the Borland-Dennis inequality [14, 15, 19, 24]. In contrast, the singlet ground states of even-electron quantum systems are not pinned to the generalized Pauli constraints [14, 24]; in fact, the generalized Pauli constraints for even-electron quantum states with singlet spin symmetry, or more generally time-reversal symmetry, reduce to the conventional Pauli conditions [14, 24]. The one-electron ionization of the even-electron wave function, however, yields an odd-electron wave function that possesses non-trivial generalized Pauli constraints. The generalized Pauli constraints with respect to the ionized wave function can be evaluated with respect to the 2-RDM of the original unionized wave function. Computationally, we will show that the pure representability constraints of the theorem define at least parts of the boundary of the exact pure 4-representable set of 2-RDMs.

For every representation of a many-fermion quantum system, there exists by *particle-hole symmetry* an equivalent, equally valid representation in which the particles and the holes of the quantum system are exchanged. For example, with respect to the ensemble N-representability conditions of the 2-RDM, particle-hole symmetry means that both the two-particle and the two-hole RDMs must be positive semidefinite [4–6, 53]:

$$ {}^2D \succeq 0 \tag{15} $$

$$ {}^2Q \succeq 0 \tag{16} $$

where

$$ {}^2Q^{pq}_{st} = 2\delta^p_s \wedge \delta^q_t - 4\,{}^1D^p_s \wedge \delta^q_t + {}^2D^{pq}_{st}. \tag{17} $$

The δ^p_s is the Kronecker delta function and $\wedge$ is the Grassmann wedge-product operator [33, 54]. The symbol $M \succeq 0$ indicates that the matrix M is positive semidefinite. A matrix is *positive semidefinite* if and only if its eigenvalues are nonnegative. By particle-hole symmetry, we have the following corollary to the theorem:

Corollary: By particle-hole symmetry, in addition to the constraints in the above, a pure N-representable 2-RDM corresponding to a wave function Ψ in the space $\wedge^N_r H$ must also satisfy the following constraints:

$$ \mathrm{Tr}({}^1\hat{O}_m \, {}^1\tilde{Q}) \geq 0 \; \forall {}^1\hat{O}_m \in B^1_{r-N-1,r-1} \tag{18} $$

in which

$$ {}^1\tilde{Q}^q_t = \kappa \sum_{p,s} c^*_p \, {}^2Q^{pq}_{st} \, c_s \tag{19} $$

where the effective 1-RDM ${}^1\tilde{Q}$ is expressible in terms of the 2-hole RDM ${}^2Q$, the arbitrary parameters c_s, and the constant κ that normalizes ${}^1\tilde{Q}$ to $(r-N-1)$. The proof of corollary is identical to the proof of the theorem with the roles of particles and holes reversed. Physically, these constraints correspond to testing generalized Pauli constraints with respect to wave functions formed by the removal of a hole.

The pure N-representability conditions can be readily extended to p-fermion RDMs where $p > 2$. For example, the pure N-representability conditions of the 3-RDM can be derived from considering the following three types of modified wave functions:

$$ |\tilde{\Psi}\rangle = \left(\sum_{st} c_{st} \hat{a}_s \hat{a}_t \right) |\Psi\rangle \tag{20} $$

$$ |\tilde{\Psi}\rangle = \left(\sum_{st} c_{st} \hat{a}^\dagger_s \hat{a}_t \right) |\Psi\rangle \tag{21} $$

$$ |\tilde{\Psi}\rangle = \left(\sum_{st} c_{st} \hat{a}^\dagger_s \hat{a}^\dagger_t \right) |\Psi\rangle \tag{22} $$

which correspond to $(N-2)$-, N-, and $(N+2)$-particle wave functions, respectively. Evaluation of the generalized Pauli constraints with respect to each of these three types of wave functions can be accomplished from a knowledge of the original wave function's 3-RDM. Therefore, as in the theorem for the 2-RDM, we have a large class of pure N-representability conditions on the 3-RDM. Similarly, we can act on the original wave function with a general polynomial in $(p-1)$ second-quantized operators to generate pure N-representability conditions on the p-RDM.

III. APPLICATIONS

The derived pure N-representability conditions on the 2-RDM are applied to a family of four-electron molecules in eight orbitals including linear and square H_4, He_2, HeH^-, Be_2, and BeB^+. Each of the molecules is treated in the Slater-type orbital (STO-6G) basis set [55] except for He_2 and HeH^- which are treated in the 6-31G basis set [56]. Bond distances are consistently set to 1.2 Å.

TABLE II. For a family of 4-electron molecules we report the distance from the FCI 2-RDM (1-RDM) to the most saturated constraint (facet) of the approximate pure 2-RDM set (exact pure 1-RDM set). For all molecules while the 1-RDMs of the singlet ground states of the four-electron molecules are not pinned to the generalized Pauli constraints, the 2-RDMs are pinned to at least one of the necessary pure N-representability conditions in Eqs. (6) and (18).

	Correlation	Distance to the Most Saturated Facet	
Molecule	Energy	Pure 1-RDM Set	Pure 2-RDM Set
H_4(l)	-0.099861	0.034475	1.05×10^{-13}
H_4(s)	-0.263197	0.047194	6.04×10^{-14}
He_2	-0.029180	0.003631	2.92×10^{-14}
HeH^-	-0.024936	0.004020	3.04×10^{-16}
Be_2	-0.075794	0.001086	7.00×10^{-14}
BeB^+	-0.107221	0.001247	8.51×10^{-14}

TABLE III. For approximate 2-RDMs of 4-electron molecules from variational calculations with D, Q, and G conditions, we report the distance of the 2-RDM (1-RDM) to the most violated constraint (facet) of the approximate pure 2-RDM set (exact pure 1-RDM set). While for all molecules the generalized Pauli constraints describing the pure 1-RDM set are not violated (positive distances), the necessary pure N-representability conditions in Eqs. (6) and (18) are significantly violated (negative distances).

	Correlation	Distance to the Most Violated Facet	
Molecule	Energy	Pure 1-RDM Set	Pure 2-RDM Set
H_4(l)	-0.103306	0.036652	-0.038903
H_4(s)	-0.270976	0.048713	-0.157273
He_2	-0.029220	0.003647	-0.002336
HeH^-	-0.025011	0.004027	-0.005478
Be_2	-0.076187	0.001270	-0.004230
BeB^+	-0.107375	0.001337	-0.011253

Core orbitals and the p_x and p_y orbitals of Be and B are excluded. Both exact and approximate 2-RDMs are computed. The exact 2-RDMs are obtained from the ground-state wave function from diagonalization of the four-electron Hamiltonian, known as full configuration interaction (FCI), and the approximate 2-RDMs are obtained from variational calculations of the 2-RDM [6, 34–51] subject to the necessary ensemble N-representability conditions, known as the D, Q, and G constraints [26, 28]. The degree of pinning of the 2-RDM to a set of constraints is assessed by reporting the distance of the effective 1-RDM in Eqs. (7) and (19) to the most saturated constraint (facet of the set). If an approximate 2-RDM violates one or more constraints, we report the distance to the most violated constraint (facet of the set) with the distance being given a negative sign to indicate that the 2-RDM lies outside the set described by the constraint. The most saturated or violated constraint is identified by (*i*) minimizing the residual of each inequality in Eqs. (6) and (18) with respect to the parameters in the effective 1-RDM and (*ii*) selecting the constraint in (*i*) that has the minimum residual. We use the Euclidean ℓ_2 metric [57] to define the distance to the boundary of each set (other metrics such as the ℓ_1 metric, the trace distance, or the Bures metric, which is related to quantum fidelity, can also be employed [58]).

For a family of four-electron molecules Table II reports the distance from the FCI 2-RDM (1-RDM) to the most saturated constraint (facet) of the approximate pure N-representable 2-RDM set (exact pure 1-RDM set). While the 1-RDMs of the singlet ground states of the four-electron molecules are not pinned to the generalized Pauli constraints, the 2-RDMs of all 6 molecules are pinned to at least one of the necessary pure N-representability conditions in Eq. (6) [or (18)]. The results are not sensitive to the distance metric chosen; for example, the 2-RDMs are pinned to the pure conditions of the 2-RDM with respect to any metric. These 2-RDM conditions are generalized Pauli constraints for 3 electrons in 7 orbitals (or 5 electrons in 7 orbitals) in Table II applied to the effective 1-RDMs in Eq. (7) [or (19)]. The addition or subtraction of an electron changes the singlet even-electron wave function to a non-singlet odd-electron wave function where the generalized Pauli constraints do not reduce to the Pauli constraints and hence, the 2-RDM conditions are non-trivial. Furthermore, the pinning of the ground-state FCI 2-RDMs to one or more of the pure 2-RDM conditions demonstrates that at least for 4-electron systems the necessary conditions describe a pure 2-RDM set whose boundary intersects significantly with the exact pure 2-RDM set.

The variational calculation of the 2-RDM with respect to necessary N-representability conditions yields an energy that is a lower bound to the FCI ground-state energy [6]. The energy is a rigorous lower bound because the 2-RDM is optimized with respect to a set of 2-RDMs that is larger than the set of N-representable 2-RDMs. For approximate 2-RDMs of 4-electron molecules from variational calculations with D, Q, and G conditions, Table III reports the distance of the 2-RDM (1-RDM) to the most violated constraint (facet) of the approximate pure 2-RDM set (exact pure 1-RDM set). For all six molecules the generalized Pauli constraints describing the pure 1-RDM set are not violated, as indicated by the positive distances. In fact, the data shows that the 1-RDMs from the D, Q, and G constraints in Table III are less pinned to the generalized Pauli constraints than the exact 1-RDMs in Table II. In contrast, for all molecules the necessary pure N-representability conditions describing the approximate pure 2-RDM set are significantly violated, as evidenced by the negative distances. These violations are not sensitive to the distance metric chosen. Consequently, the necessary pure N-representability conditions on the 2-RDM in Eqs. (6) and (18) provide stringent N-representability conditions beyond the ensemble D, Q, and G conditions. Preliminary calculations on BeB^+ at 4 Å where ensemble DQG conditions have difficulty indicate that the iterative addition of the most violated constraint raises the correlation energy from its DQG lower bound towards its FCI value. After the addition of 22 pure constraints to the DQG conditions, for example, the error in the correlation energy is reduced from -0.008 a.u. to -0.00031 a.u.

IV. CONCLUSIONS

Necessary pure N-representability conditions have been derived for the 2-RDM as well as higher-order p-RDMs where $p > 2$. Importantly, these conditions extend the pure N-representability conditions on the 1-RDM, also known as the generalized Pauli constraints [4, 7–25]. The pure 2-RDM conditions are derived as generalized Pauli constraints on effective 1-RDMs that are parameterized by the removal or addition of a fermion from the N-fermion wave function. Conditions on the higher p-RDMs correspond to applying general polynomials of $(p-1)$ second-quantized operators to the N-fermion wave function. The pure N-representability conditions on the 2-RDM are important because they provide stringent constraints beyond those from the Pauli and generalized Pauli constraints on the structure of many-fermion ground-state 2-RDMs and their wave functions. These constraints have potentially significant applications to computing strongly correlated many-fermion states with a decreased computational complexity, i.e. as in the direct variational computation of the 2-RDM with approximate N-representability conditions [6, 34–51]. They are applicable to strongly correlated molecules as well as model spin systems such as the Hubbard model. Computationally, we showed for 4-electron molecules that the derived pure N-representability conditions non-trivially pin (or expose) the exact FCI 2-RDMs and that they provide significant restrictions beyond the D, Q, and G ensemble N-representability conditions. Pure N-representability conditions on the 2-RDM and higher-order p-fermion RDMs provide new insight into the generalization of the Pauli exclusion principle by Heisenberg [2] and Dirac [3] as well as novel implications for the description of electron correlation and entanglement in physics and chemistry.

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