Geometric constraints on two-electron reduced density matrices

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For many-electron systems, the second-order reduced density matrix (2-RDM) provides sufficient information for characterizing their properties of interests in physics and chemistry. In this paper, we present a set of nontrivial constraints on 2-RDM based on the basic geometric property of Hilbert space and the commutation relations of operators. Numerical examples are provided to demonstrate the pronounced violation of these constraints by the variational 2-RDMs. It is shown that, for a strongly correlated model system, the constraint violation may be responsible for a considerable portion of the variational error in ground-state energy. Our findings provide new insights into the structural subtlety of many-electron 2-RDMs.

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I. INTRODUCTION

In 1930, Paul Dirac introduced the idea of utilizing the reduced density matrix (RDM) to approximate the properties of many-electron systems in order to avoid intractable computation of many-electron wave function [1]. The research efforts in this direction led to the development of various electronic structure theories based on one- and two-electron RDMs (1-RDMs and 2-RDMs) [2–16]. Among these approaches, density-functional theory (DFT) is most successful and popular [5–7,9]. In DFT, the ground-state energy of interacting electrons can be expressed as an energy functional of one-electron density based on the Hohenberg–Kohn theorem. For practical DFT calculations, the energy functional can be approximated to provide sufficient accuracy with low computational cost for most of quantum physics and chemistry applications. A major challenge in DFT is to systematically improve energy functional approximations for describing strongly correlated systems [9,10,17–19].

In parallel, the approaches based on high-order RDMs have been actively pursued aiming at the systems with strongly correlated electrons or nuclei [2–4,11–13,20,21]. In these approaches, the energy expression is exact. However, it is difficult to find sufficient constraints on an approximated RDM in order to ensure its correspondence to a many-electron wave function [12]. In quantum chemistry, this problem is known as N-representability problem [11], a special case of quantum marginal problem in quantum information [22]. For strongly correlated systems, this problem may cause predicting erroneous bond dissociation barriers and unphysical properties such as fractional charges and fractional spins [23–29]. Since the problem was formalized in the early 1960s, substantial research efforts have been made to identify sufficiently stringent N-representability constraints and to implement them in practical computations. The progress has been steady but slow due to its challenging mathematical and computational nature [11–13,22,30,31]. With recent exciting developments in quantum computing and information technologies, this problem is attracting more attention now because of the key role of quantum marginals in quantum measurement and information processing [30,32–42].

Currently, most nontrivial N-representability constraints originate from two basic properties of a state in fermion Hilbert space: antisymmetric permutation [43–45] and the fact that inner product of the state with itself is non-negative. The symmetry property imposes an upper bound on the eigenvalues of 1-RDMs (Pauli principle) and an antisymmetric condition on electron and hole 2-RDMs [11]. A major breakthrough on the quantum marginal problem has been made by Klyachko utilizing representation theory of symmetric group, which leads to a family of constraints on the eigenvalues of pure-state 1-RDMs (generalized Pauli constraints) [22,33–35,37,46–49]. Based on generalized Pauli constraints, pure-state constraints on 2-RDMs have been proposed recently [50].

The non-negativity inner product property requires any RDM to be Hermitian and positive semidefinite, which implies a set of the most restrictive constraints currently utilized in practical 2-RDM-based calculations. This set of constraints includes D, Q, G, $T1$, $T2$, and $T2'$ conditions. The positive-semidefinite constraints on the 2-RDM and its variants (D, Q, and G conditions) were proposed by Coleman [11] and Garrod and Percus [51] in the early 1960s. In 1978, Erdahl discovered $T1$ and $T2$ conditions by introducing a clever idea to reduce the 3-RDM positive-semidefinite conditions to a set of conditions on 1-RDMs and 2-RDMs [52]. The more restrictive $T2'$ condition was reduced from the positive-semidefinite condition on a variant of 3-RDMs [53,54]. Inspired by this idea, Mazziotti developed a systematic approach to deduce 2-RDM conditions from higher-order RDM constraints and proved in 2012 that inclusion of the whole set of deduced conditions sufficiently ensures a 2-RDM to be N representable [55]. However, the number of the deduced conditions increases exponentially with the many-body order of the RDM. It is not

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yet clear how the effectiveness of these conditions depends on the order increase.

At present, the variational 2-RDM method is one of most promising high-order RDM approaches. In this approach, the positive-semidefinite conditions can be implemented by either positive-semidefinite programming (SDP) [56] or nonlinear optimization [57]. For many molecular systems with up to 28 electrons, the accuracy of the variational ground-state energy is comparable to the high-level wave-function-based method CCSD(T) [53,58]. More recently, the effects of strong correlation in a range of large molecular complexes have been unveiled using variational 2-RDM calculations with D, Q, and G conditions [59,60]. These applications to systems intractable with conventional wave-function-based methods further demonstrate the great potential of 2-RDM-based approaches. On the other hand, for strongly correlated systems, such as one-dimensional (1D), quasi-two-dimensional (quasi-2D), and 2D Hubbard models [28,58,61–63], the Lipkin model [54], molecule chains [38,57,64], and the molecules near dissociation limit [26,27,65,66], the variational results are encouraging but their deviations from exact results still cannot be ignored in many cases. Evidently, a more restrictive constraint is in demand to elucidate the intriguing physical and chemical properties of strongly correlated systems.

In this paper, we present a set of geometric constraints for characterizing the N-representable 2-RDMs. Our analysis is based on the basic geometric property of Hilbert space, the triangle inequality, and the commutation relations of operators in fermion Hilbert space. These constraints are explicitly imposed on the eigenvalues and eigenvectors of fermion 2-RDMs. Numerical examples are provided to demonstrate the evident violation of these constraints by variational 2-RDMs, even in the case where the error in the variational ground-state energy is negligibly small. It is also shown that, for a strongly correlated system, the constraint violation by variational 2-RDMs may contribute a large portion of its error in the ground-state energy. Based on basic geometric properties of Hilbert space, our analysis is concise without direct involvement of higher-order RDMs, and is applicable for tackling quantum marginal problems in general.

II. TWO-ELECTRON REDUCED DENSITY MATRIX AND LIE ALGEBRA

A. The eigenoperators of reduced density matrices and their Lie algebra properties

We start with some necessary notation. For a given wave function $|\Psi\rangle$ in N-electron Hilbert space, the 2-RDMs D, G, and Q are defined as [12]

$$D_{ij,kl} = \langle\Psi|a_i^\dagger a_j^\dagger a_l a_k|\Psi\rangle, \tag{1a}$$

$$G_{ij,kl} = \langle\Psi|a_i^\dagger a_j a_l^\dagger a_k|\Psi\rangle, \tag{1b}$$

and

$$Q_{ij,kl} = \langle\Psi|a_i a_j a_l^\dagger a_k^\dagger|\Psi\rangle. \tag{1c}$$

Here $a_i^\dagger$ and a_i are the electron creation and annihilation operators associated with single-electron basis

$$\{|\phi_i\rangle,\ i = 1, 2, \ldots, L\},$$

respectively. The creation and annihilation operators obey the anticommutative rules. D, G, and Q are $L^2 \times L^2$ matrices. They are interconnected according to the anticommutation relations of creation and annihilation operators. The D and Q matrices are antisymmetric: $D_{ij,kl} = -D_{ji,kl} = -D_{ij,lk}$ and $Q_{ij,kl} = -Q_{ji,kl} = -Q_{ij,lk}$.

These three matrices are Hermitian and positive semidefinite and can be diagonalized as

$$D_{ij,kl} = \sum_{n=1}^{\frac{L(L-1)}{2}} u_{ij}^{n*} \lambda_n^D u_{kl}^n, \tag{2a}$$

$$G_{ij,kl} = \sum_{n=1}^{L^2} v_{ij}^{n*} \lambda_n^G v_{kl}^n, \tag{2b}$$

and

$$Q_{ij,kl} = \sum_{n=1}^{\frac{L(L-1)}{2}} w_{ij}^{n*} \lambda_n^Q w_{kl}^n. \tag{2c}$$

Here, λ_n^D, λ_n^G, and λ_n^Q are, respectively, the nth eigenvalues of the D, G, and Q matrices with corresponding eigenvectors u_{ij}^n, v_{ij}^n, and w_{ij}^n.

Using the eigenvectors, we define the eigenoperators of RDMs. For the D matrix, its nth eigenoperator d_n is defined by

$$d_n = \sum_{i,j=1}^{L} u_{ij}^n a_j a_i. \tag{3a}$$

$\mathfrak{s}_D$ denotes the eigenoperator set $\{d_n,\ n = 1, 2, \ldots, \frac{L(L-1)}{2}\}$. Similarly, for the G and Q matrices, we have

$$g_n = \sum_{i,j=1}^{L} v_{ij}^n a_j^\dagger a_i,$$

$$\mathfrak{s}_G = \{g_n,\ n = 1, 2, \ldots, L^2\}, \tag{3b}$$

and

$$q_n = \sum_{i,j=1}^{L} w_{ij}^n a_j^\dagger a_i^\dagger, \tag{3c}$$

$$\mathfrak{s}_Q = \left\{q_n,\ n = 1, 2, \ldots, \frac{L(L-1)}{2}\right\}.$$

Based on Eqs. (2a)–(2c), the eigenoperators have the properties

$$\langle\Psi|d_m^\dagger d_n|\Psi\rangle = \lambda_m^D \delta_{mn}, \tag{4a}$$

$$\langle\Psi|g_m^\dagger g_n|\Psi\rangle = \lambda_m^G \delta_{mn}, \tag{4b}$$

and

$$\langle\Psi|q_m^\dagger q_n|\Psi\rangle = \lambda_m^Q \delta_{mn}, \tag{4c}$$

where δ_{mn} is the Kronecker delta.

The eigenoperators of RDMs are pair operators. Their commutation relations are

$$[g_m, g_n] = \sum_{m'=1}^{L^2} \Gamma_{mn}^{m'} g_{m'}, \tag{5a}$$

$$[g_m, d_n] = \sum_{m'=1}^{\frac{L(L-1)}{2}} \Delta_{mn}^{m'} d_{m'}, \tag{5b}$$

$$[g_m, q_n] = \sum_{m'=1}^{\frac{L(L-1)}{2}} \Omega_{mn}^{m'} q_{m'}, \tag{5c}$$

$$[q_m, d_n] = \sum_{m'=1}^{L^2} \Theta_{mn}^{m'} g_{m'}, \tag{5d}$$

and

$$[d_m, d_n] = [q_m, q_n] = 0. \tag{5e}$$

Here the coefficients are given by

$$\Gamma_{mn}^{m'} = \sum_{i,j,k=1}^{L} \left(v_{kj}^m v_{ik}^n - v_{ik}^m v_{kj}^n\right) v_{ij}^{m'*}, \tag{6a}$$

$$\Delta_{mn}^{m'} = -2 \sum_{i,j,k=1}^{L} v_{ik}^m u_{kj}^n u_{ij}^{m'*}, \tag{6b}$$

$$\Omega_{mn}^{m'} = 2 \sum_{i,j,k=1}^{L} w_{ik}^n v_{kj}^m w_{ij}^{m'*}, \tag{6c}$$

and

$$\Theta_{mn}^{m'} = 4 \sum_{i,j,k=1}^{L} \left(u_{ik}^m w_{kj}^n v_{ij}^{m'*} - \frac{1}{2N} u_{ij}^m w_{ji}^n v_{kk}^{m'*}\right). \tag{6d}$$

In the derivation of these commutation relations (see Appendix for detail), we have used the facts that $u_{ij}^m = -u_{ji}^m$, and $w_{ij}^m = -w_{ji}^m$. For Eq. (6d), we have restricted ourselves to the N-electron Hilbert space. From these commutation relations, we can see that the eigenoperators of RDMs form a complete basis set of a Lie algebra. We denote this Lie algebra by $\mathfrak{h}$. Furthermore, $\mathfrak{s}_G$ is a subalgebra of $\mathfrak{h}$.

The commutators in Eqs. (5a)–(5d) maps the state $|\Psi\rangle$ to four unnormalized vectors in Hilbert space. The length of these vectors are given by

$$\alpha_{mn} = (\langle\Psi|([g_m, g_n])^\dagger [g_m, g_n]|\Psi\rangle)^{\frac{1}{2}} = \left(\sum_{m'=1}^{L^2} \left|\Gamma_{mn}^{m'}\right|^2 \lambda_{m'}^G\right)^{\frac{1}{2}}, \tag{7a}$$

$$\beta_{mn} = (\langle\Psi|([q_m d_n])^\dagger [q_m d_n]|\Psi\rangle)^{\frac{1}{2}} = \left(\sum_{m'=1}^{L^2} \left|\Theta_{mn}^{m'}\right|^2 \lambda_{m'}^G\right)^{\frac{1}{2}}, \tag{7b}$$

$$\gamma_{mn} = (\langle\Psi|([g_m d_n])^\dagger [g_m d_n]|\Psi\rangle)^{\frac{1}{2}} = \left(\sum_{m'=1}^{\frac{L(L-1)}{2}} \left|\Delta_{mn}^{m'}\right|^2 \lambda_{m'}^D\right)^{\frac{1}{2}}, \tag{7c}$$

and

$$\zeta_{mn} = (\langle\Psi|([g_m q_n])^\dagger [g_m q_n]|\Psi\rangle)^{\frac{1}{2}} = \left(\sum_{m'=1}^{\frac{L(L-1)}{2}} \left|\Omega_{mn}^{m'}\right|^2 \lambda_{m'}^Q\right)^{\frac{1}{2}}. \tag{7d}$$

These lengths will be used later for verifying the effectiveness of N-representability constraints.

B. The null eigenoperators of reduced density matrices

An operator is called a null operator of a wave function if it maps the wave function to a null vector. For a given wave function, the commutator of two null operators must be a null operator. Therefore, all the null operators of a given wave function form a Lie algebra.

In the Lie algebra $\mathfrak{h}$, we define a subset $\mathfrak{n} = \{p \in \mathfrak{h} : \forall\ p|\Psi\rangle = 0\}$. Apparently, $\mathfrak{n}$ is a subalgebra of $\mathfrak{h}$. For any operator

$$p = \sum_{i,j=1}^{L} (r_{ij} a_j a_i + s_{ij} a_j^\dagger a_i + t_{ij} a_j^\dagger a_i^\dagger) \tag{8}$$

in $\mathfrak{n}$, we have

$$\begin{aligned} 0 &= \langle\Psi|p^\dagger p|\Psi\rangle \\ &= \sum_{ijkl} (r_{ij}^* r_{kl} \langle\Psi|a_i^\dagger a_j^\dagger a_l a_k|\Psi\rangle + s_{ij}^* s_{kl} \langle\Psi|a_i^\dagger a_j a_l^\dagger a_k|\Psi\rangle \\ &\quad + t_{ij}^* t_{kl} \langle\Psi|a_i a_j a_l^\dagger a_k^\dagger|\Psi\rangle) \\ &= \sum_{ijkl} (r_{ij}^* r_{kl} D_{ij,kl} + s_{ij}^* s_{kl} G_{ij,kl} + t_{ij}^* t_{kl} Q_{ij,kl}), \end{aligned}$$

which implies

$$\sum_{ijkl} r_{ij}^* D_{ij,kl} r_{kl} = \sum_{ijkl} s_{ij}^* G_{ij,kl} s_{kl} = \sum_{ijkl} t_{ij}^* Q_{ij,kl} t_{kl} = 0, \tag{9}$$

since the D, G, and Q matrices are positive semidefinite. Equation (9) shows that the vectors r_{ij}, s_{ij}, and t_{ij} are in the null space of matrices D, G, and Q, respectively. They can be expanded by linear combinations of the eigenvectors in the null space of RDMs as

$$r_{ij} = \sum_{m=1}^{N_{\text{null}}^D} c_m^r u_{ij}^m, \tag{10a}$$

$$s_{ij} = \sum_{m=1}^{N_{\text{null}}^G} c_m^s v_{ij}^m, \tag{10b}$$

and

$$t_{ij} = \sum_{m=1}^{N_{\text{null}}^Q} c_m^t w_{ij}^m, \tag{10c}$$

where the expansion coefficients are given by $c_m^r = \sum_{i,j=1}^{L} u_{ij}^{m*} r_{ij}$, $c_m^s = \sum_{i,j=1}^{L} v_{ij}^{m*} s_{ij}$, and $c_m^t = \sum_{i,j=1}^{L} w_{ij}^{m*} t_{ij}$. N_{null}^D, N_{null}^G, and N_{null}^Q are the dimension of the null spaces of matrices D, G, and Q, respectively. m is the index for the corresponding null eigenvector of RDMs.

Substituting Eqs. (10a)–(10c) into Eq. (8), we have the expansion for operator p as

$$p = \sum_{m=1}^{N_{\text{null}}^{D}} c_m^r d_m + \sum_{m=1}^{N_{\text{null}}^{G}} c_m^s g_m + \sum_{m=1}^{N_{\text{null}}^{Q}} c_m^t q_m. \tag{11}$$

We call an eigenoperator the null eigenoperator of RDM if its associated eigenvector is in the null space of the RDM. Equation (11) indicates that the set of all null eigenoperators must form a complete basis set of the subalgebra $\mathfrak{n}$. Similarly, it can be shown that the operator vector space $\mathfrak{n}_G$ spanned by the null eigenoperators of G matrix must be a subalgebra of $\mathfrak{n}$.

III. CONSTRAINTS ON NULL SPACES OF SECOND-ORDER REDUCED DENSITY MATRICES

The requirement that all null eigenoperators form a Lie algebra imposes a set of nontrivial constraints on the null spaces of 2-RDMs. For two null eigenoperators g_m, g_n of the G matrix and their commutator $[g_m, g_n]$, using Eq. (3b) we have (see Appendix for detail)

$$[g_m, g_n]|\Psi\rangle = \sum_{i,j=1}^{L} v_{ij}^{mn} a_j^\dagger a_i |\Psi\rangle, \tag{12}$$

where

$$v_{ij}^{mn} = \sum_{k=1}^{L} \left(v_{kj}^m v_{ik}^n - v_{ik}^m v_{kj}^n\right). \tag{13}$$

The length of vector $[g_m, g_n]|\Psi\rangle$ vanishes, and we have

$$\begin{aligned} 0 =& \langle\Psi|([g_m, g_n])^\dagger [g_m, g_n]|\Psi\rangle \\ =& \sum_{i,j,k,l=1}^{L} \left(v_{ij}^{mn}\right)^* G_{ij,kl} v_{kl}^{mn}, \end{aligned} \tag{14}$$

which indicates that $\boldsymbol{v}^{mn}$ must be in the null space of the G matrix. This requirement imposes a constraint on the null space of the G matrix.

If d_m and q_n are, respectively, the null eigenoperators of the D and Q matrices, we can derive the constraint on the null spaces of D and Q matrices:

$$0 = \sum_{i,j,k,l=1}^{L} \left(\overline{v}_{ij}^{mn}\right)^* G_{ij,kl} \overline{v}_{kl}^{mn}, \tag{15}$$

here

$$\overline{v}_{ij}^{mn} = 4\left(\sum_{k=1}^{L} u_{ik}^m w_{kj}^n - \frac{1}{2N} \sum_{k,k'=1}^{L} u_{kk'}^m w_{k'k}^n \delta_{ij}\right). \tag{16}$$

More constraints on the null spaces can be found by using the commutation relations (5b) and (5c). They are

$$0 = \sum_{i,j,k,l=1}^{L} \left(\overline{u}_{ij}^{mn}\right)^* D_{ij,kl} \overline{u}_{kl}^{mn}, \tag{17}$$

with

$$\overline{u}_{ij}^{mn} = -2 \sum_{k=1}^{L} v_{ik}^m u_{kj}^n, \tag{18}$$

and

$$0 = \sum_{i,j,k,l=1}^{L} \left(\overline{w}_{ij}^{mn}\right)^* Q_{ij,kl} \overline{w}_{kl}^{mn}, \tag{19}$$

with

$$\overline{w}_{ij}^{mn} = 2 \sum_{k=1}^{L} w_{ik}^n v_{kj}^m. \tag{20}$$

These constraints are equivalent to the conditions that the lengths given in Eqs. (7a)–(7d) vanish for the commutators of two null eigenoperators. They show why the positive-semidefinite conditions are not strong enough for N-representability problem.

IV. NUMERICAL VERIFICATION OF CONSTRAINT EFFECTIVENESS

To examine the effectiveness of the constraints on the null space numerically, we employ a variational 2-RDM method to obtain approximated 2-RDMs of the ground state. In the variational 2-RDM method, the total energy of a system is a function of the D matrix, $E = \text{tr}(KD)$. Here, K is the Hamiltonian matrix of the system. The ground-state energy of the system is obtained by variationally minimizing the total energy with respect to the D matrix under the restriction of N-representability constraints. The currently available conditions are not restrictive enough to constrain the variational 2-RDM (D_{var}). Therefore, the variational energy E_{var} provides a low-boundary estimation of the ground-state energy. The variational 2-RDM method has been utilized routinely in the past to demonstrate the effectiveness of N-representability conditions [50,53,56,58,67–69]. In numerical tests, we perform variational 2-RDM method first to obtain E_{var} and D_{var}, and calculate the variational G and Q matrices (G_{var} and Q_{var}) from D_{var}. Then, the eigenvalues and eigenvectors of D_{var}, G_{var}, and Q_{var} are used to check whether the constraints given in previous section are held by the variational 2-RDMs. In the variational 2-RDM calculations, we have applied D, Q, G, $T1$, $T2$, and $T2'$ conditions [53,58], which, to the best of our knowledge, are the most restrictive constraints currently available for practical computation.

In this section, the numerical studies serve two purposes: First, we would like to rigorously exam the tightness of the new constraints with respect to D, Q, G, $T1$, $T2$, and $T2'$ conditions. Second, we want to estimate how much the error in the null eigenspace of the variational 2-RDMS may contribute to the energy deviation of the variational ground state from the exact result. The variational RDMs are calculated for several systems: a one-dimensional Hubbard model, a diatomic molecule LiH, and two random-matrix Hamiltonians with free spin. The numerical results are summarized in Table I. To reduce the number of variational variables and to improve numerical accuracy, the linear equalities derived from the symmetries of specific systems are solved explicitly before the variational calculation. For comparison, the exact RDMs are also calculated by the full configuration-interaction method (FCI). Variational calculations are carried out using a SDP software, Sedumi 1.3 [70]. According to the "prec" parameter in Sedumi output, the numerical accuracy is about

TABLE I. Summary of numerical tests for four systems: Hubbard Model with $U/t = 10$, diatomic molecule LiH, and two random matrix Hamiltonians. L and N_e are the number of single-particle basis and electrons in the system, respectively. The number of null eigenoperators (NEO) for variational D_{var}, G_{var}, and Q_{var} matrices are shown with the number for exact RDMs given in parentheses for comparison. ΔE is the deviation of variational ground-state energy from the exact value. $\Delta E_{\text{null}}/|\Delta E|$ is an estimation for the contribution of the null space of D_{var} to the ground-state-energy deviation ΔE. I_α, I_β, I_γ, and I_ζ are four descriptors to quantify the extent that the N-representability constraints are violated by variational RDMs. For N-representable RDMs, these descriptors should vanish.

	Hubbard model	LiH	Random 1	Random 2
L	12	12	12	12
N_e	6	4	6	6
No. of NEOs of D	6 (1)	2 (0)	1 (0)	4 (0)
No. of NEOs of G	8 (3)	5 (13)	7 (3)	7 (3)
No. of NEOs of Q	6 (1)	1 (0)	3 (0)	1 (0)
ΔE	-3.1×10^{-2}	$-1.7 \times 10^{-8}\, E_h$	-1.3×10^{-1}	-1.3×10^{-2}
$\Delta E_{\text{null}}/\lvert\Delta E\rvert$	42%	−67%[1]	4.2%	6.5%
I_α	0.78×10^{-2}	0	0.19×10^{-1}	0.78×10^{-2}
I_β	0.21×10^{-1}	0.30×10^{-3}	0.43×10^{-1}	0.21×10^{-1}
I_γ	0.15×10^{-1}	0.87×10^{-4}	0.16×10^{-1}	0.15×10^{-1}
I_ζ	0.14×10^{-1}	0.12×10^{-3}	0.46×10^{-1}	0.14×10^{-1}

[1]This value is problematic because, for LiH, ΔE_{null} and $|\Delta E|$ are both on the order of 10^{-8} and are close to the numerical accuracy of variational calculation ($\approx 10^{-9}$).

10^{-9} in variational calculations, so we regard any value in $(-10^{-9}, 10^{-9})$ as numerical zero.

A. Hubbard model

The Hubbard model is a prototype system for studying strongly correlated electrons [71]. Here, the system is a six-site half filled 1D Hubbard model with periodic boundaries, $t = 1$ and varying U. For $U/t = 10$, the ground-state energies obtained by the FCI and the variational 2-RDM method are $E_{\text{exact}} = -1.664\,362\,733\,287$ and $E_{\text{var}} = -1.695\,384\,327\,725$, respectively. Compared with E_{exact}, the energy deviation $\Delta E = -0.031\,021\,594\,438$. These energies are consistent with the previous studies on this model [58].

For the exact RDMs in Table II, the eigenvalues of D_{exact} and Q_{exact} matrix have one null eigenoperator each, corresponding to the pseudospin operator and its conjugate transpose, which is known for a half filled Hubbard model [72]. The three null eigenvalues of the G_{exact} matrix correspond to the three spin operators, s_x, s_y, and s_z because the ground state of the half filled Hubbard model is a singlet.

Comparing with D_{exact}, there are five more null eigenoperators for D_{var} (Table II). The ground-state energy $E = \text{tr}(KD)$ with K being the Hamiltonian matrix, so the six-dimensional null space of D_{var} has no contribution to the variational ground-state energy, E_{var}. To roughly assess how much the null space of D_{var} contributes to the deviation of ground-state energy ΔE, we first project D_{exact} onto the six-dimensional (6D) null space and then calculate the energy contribution of the projected D matrix. Let $P = \sum_{n=1}^{6} \mathbf{u}_n \mathbf{u}_n^T$ be the projection matrix, where $\mathbf{u}_n$, $n = 1, 2, \ldots, 6$ are the eigenvectors in the null space of D_{var}. Then, the energy contribution

$$\begin{aligned} \Delta E_{\text{null}} &= \text{tr}(KPD_{\text{exact}}P) \\ &= 0.013\,134\,139\,307. \end{aligned} \tag{21}$$

The positive value of ΔE_{null} indicates that the erroneous null space causes the underestimation of ground-state energy by D_{var}. Its contribution to the energy deviation is quite large,

TABLE II. The ten lowest eigenvalues of the variational and exact RDMs for a six-site half filled 1D Hubbard model with $t = 1$ and $U = 10$. The ground-state energies obtained by the two methods are $E_{\text{exact}} = -1.664\,362\,733\,287$ and $E_{\text{var}} = -1.695\,384\,327\,725$, respectively. The energy deviation $\Delta E = -0.031\,021\,594\,438$. These energies are consistent with the previous studies on this model [58].

	D matrix		G matrix		Q matrix	
n	Variational	Exact	Variational	Exact	Variational	Exact
1	−0.000 000 000 001	−0.000 000 000 000	−0.000 000 000 000	−0.000 000 000 000	−0.000 000 000 001	0.000 000 000 000
2	−0.000 000 000 001	0.000 013 764 099	−0.000 000 000 000	−0.000 000 000 000	−0.000 000 000 001	0.000 013 764 099
3	−0.000 000 000 001	0.000 558 839 696	−0.000 000 000 000	0.000 000 000 000	−0.000 000 000 001	0.000 558 839 696
4	−0.000 000 000 001	0.000 558 839 696	−0.000 000 000 000	0.000 006 882 049	−0.000 000 000 001	0.000 558 839 696
5	−0.000 000 000 001	0.000 649 120 541	−0.000 000 000 000	0.000 279 419 848	−0.000 000 000 001	0.000 649 120 541
6	−0.000 000 000 000	0.000 649 120 541	0.000 000 000 000	0.000 279 419 848	−0.000 000 000 000	0.000 649 120 541
7	0.052 344 794 130	0.054 771 204 301	0.000 000 000 000	0.000 324 560 271	0.052 344 794 122	0.054 771 204 301
8	0.052 344 794 130	0.054 771 204 301	0.000 000 000 000	0.000 324 560 271	0.052 344 794 122	0.054 771 204 301
9	0.053 848 732 617	0.056 628 436 116	0.019 332 198 318	0.026 343 666 870	0.053 848 732 627	0.056 628 436 116
10	0.054 329 721 649	0.059 289 055 684	0.025 473 863 823	0.027 040 912 995	0.054 329 721 653	0.059 289 055 684

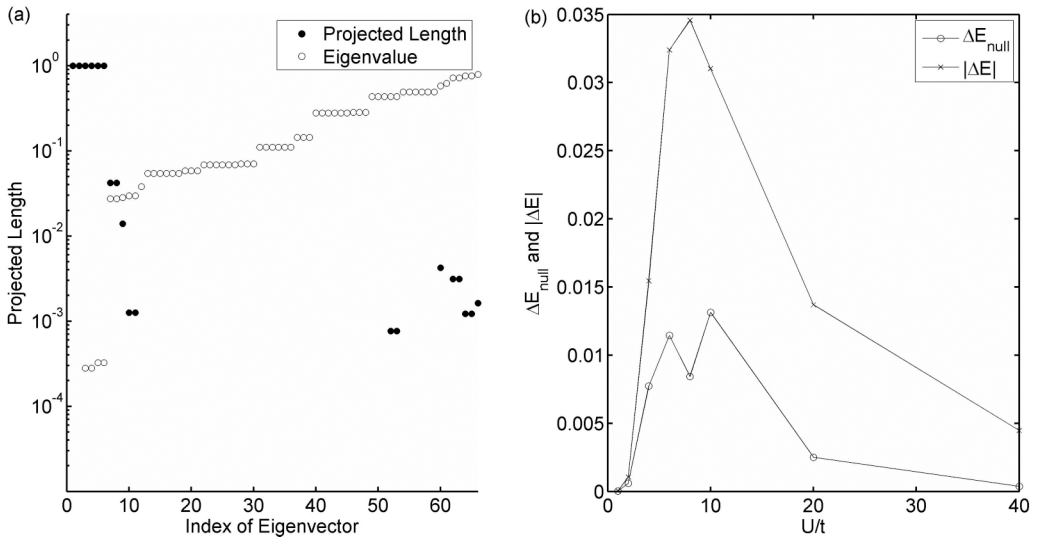

FIG. 1. (a) The projection length (filled circles) of the eigenvector of D_{exact} in the null space of D_{var} together with the corresponding eigenvalues (open circles). The eigenvalues of D_{exact} are sorted in ascending order. The results are for a 1D Hubbard model with $U/t = 10$. The null space of D_{var} has overlap with ten low-lying and eight high-lying eigenvectors of D_{exact}. (b) The contribution of the D_{var} null space to the deviation of variational total energy for 1D Hubbard model with $U/t = 1, 2, 4, 6, 8, 10, 20, 40$, respectively. The contribution is largely correlated with the deviation of variational total energy.

$\Delta E_{\text{null}}/|\Delta E| \approx 42\%$, even though its dimension is small. Figure 1(a) shows that the null space of D_{var} has overlap with not only the low-lying eigenvectors of D_{exact} but also the high-lying ones. This may explain its large contribution to the energy deviation. Furthermore, the contribution of the erroneous null space is correlated with the deviation of variational energy for the Hubbard model with varying U/t [Fig. 1(b)].

G_{var} has five more null eigenvalues than G_{exact}. As discussed in the previous section, if G_{var} is N representable, the eight corresponding null eigenoperators must form the complete basis set of a Lie algebra. That is, for two null eigenoperators g_m and g_n in $\mathfrak{n}_G$, $[g_m, g_n]|\Psi\rangle = 0$.

We use Eqs. (7a) and (7b) to verify whether the variational 2-RDMs are N representable. Figure 2(a) shows α_{mn} for the null eigenoperators of G_{var}. There are multiple nonvanishing values. Therefore, the null eigenoperators of G_{var} do not form a closed subalgebra, and G_{var} is not N representable.

Q_{var} has five more null eigenvalues than Q_{exact}. If Q_{var} and D_{var} are N representable, the commutator of their null eigenoperators must be a null eigenoperator in $\mathfrak{n}_G$. Figure 2(b) shows the β_{mn} evaluated from the null eigenoperators of Q_{var} and D_{var}. The values are on the order of 10^{-2} and, clearly, violate the N-representability constraint. The constraint violation is also prominent for the commutators of the null eigenoperators for G_{var} and D_{var} [Fig. 2(c)].

The numerical results for Hubbard model show that the constraints impose strong restrictions on the null spaces of 2-RDMs. To quantify the degree of constraint violation by variational 2-RDMs, we introduce a descriptor I_α defined as the maximum value of α_{mn} from the null eigenoperators of G. A large value of descriptor suggests strong violation. Similarly, we may define descriptors I_β, I_γ, and I_ζ for the maximum value of β_{mn}, γ_{mn}, and ζ_{mn}, respectively. The four descriptors of the Hubbard model with $U/t = 10$ are shown in Table I.

N-representability condition requires the constraints on the null spaces of 2-RDMs:

$$I_\alpha = I_\beta = I_\gamma = I_\zeta = 0. \tag{22}$$

Figure 2(d) shows the trend of constraint violation by variational 2-RDMs as U/t of Hubbard model varying. In general, we can see to $I_\beta > I_\gamma \approx I_\zeta > I_\alpha$. The maximum of these descriptors is around $U/t = 4$, which is different from that for the variational energy deviation [around $U/t = 8$, as shown in Fig. 1(b)].

B. LiH and random-matrix Hamiltonians

The violation of the null space constraint seems general for variational 2-RDM. For the diatomic molecule LiH in its equilibrium configuration, the variational method can provide the very accurate estimation of ground-state energy with $\Delta E \approx 2.0 \times 10^{-8}$ (see Table III). However, the dimensions of the null spaces of variational 2-RDMs are very different from that of the exact 2-RDMs (see Tables III and I), which indicates the disparity in the Lie algebra structure of their null eigenoperators. The descriptor $I_\beta = 0.30 \times 10^{-3}$, which is about five orders of magnitude larger than the numerical accuracy of our variational calculation.

To have a rough idea how often the variational 2-RDM method may predict erroneous null spaces of RDMs, we have applied the method to five Hamiltonians with randomly generated numbers in spatial degree of freedom. The erroneous null spaces have been found in all five cases. The results for two of them are shown in Tables IV and V. As summarized in Table I, the exact RDMs of the ground states have three null eigenoperators corresponding to three spin operators, while the variational RDMs have more null eigenoperators. The four descriptors are not vanishing for these RDMs.

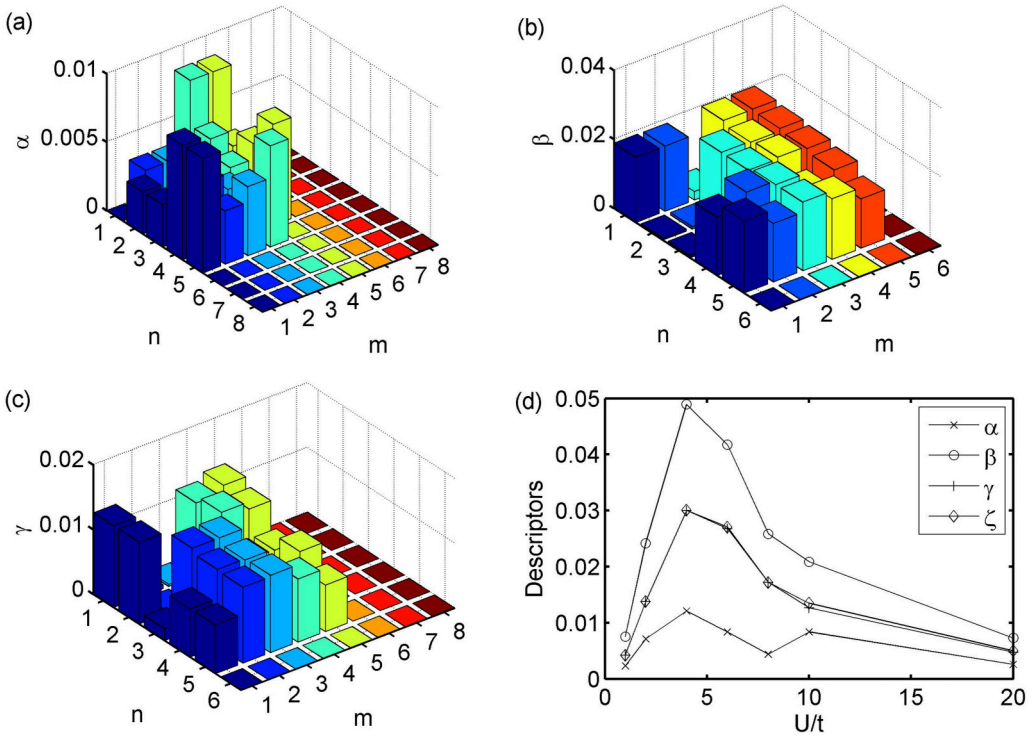

FIG. 2. The constraint test on the variational RDMs of Hubbard model. (a) The length of vector $[g_m, g_n]|\Psi\rangle$ with $m, n = 1, 2, \ldots, 8$ corresponding to the eight null eigenoperators of G_{var}. (b) The length of vector $[d_m, q_n]|\Psi\rangle$ with $m, n = 1, 2, \ldots, 6$ corresponding to the six null eigenoperators of D_{var} and Q_{var}. (c) The length of vector $[g_m, d_n]|\Psi\rangle$ with $m = 1, 2, \ldots, 8$ and $n = 1, 2, \ldots, 6$ corresponding to the eight null eigenoperators of G_{var} and six for Q_{var}. The maximal lengths in panels (a)–(c) are, respectively, about 0.0078, 0.021, and 0.015. Apparently, many of the commutators are not null operators of the state $|\Psi\rangle$, therefore D_{var}, G_{var}, and Q_{var} are not N-representable. (d) The constraint violation descriptors I_α, I_β, I_γ, and I_ζ for the Hubbard model with $U/t = 1, 2, 4, 6, 8, 10, 20, 40$. The maximum of four descriptors is around $U/t = 4$. While, the maximal deviation of variational energy is at $U/t = 8$ [see Fig. 1(b)]. Therefore, the structure deviation of the variational 2-RDM is not correlated with the error of the total energy.

From Table I, we can have two interesting observations. In contrast with the Hubbard model, a strongly correlated system, the $\Delta E_{\text{null}}/|\Delta E|$ ($\approx$5%) of the random systems is quite small, and the null space of D_{var} has very small contribution to the ground-state energy deviation ΔE. We believe $\Delta E_{\text{null}}/|\Delta E|$ (-67%) for LiH is problematic because both $|\Delta E_{\text{null}}|$ and $|\Delta E|$ are on the order of 10^{-8} and close to a numerical accuracy of 1.0×10^{-9}. For variational RDMs, the descriptors I_β, I_γ, and I_ζ are usually larger than I_α. This may suggest that the constraint on the null spaces of D and Q matrices is stronger than that on G matrix. Apparently, more numerical studies are needed in future in order to tell whether the observations are general.

V. INEQUALITY CONSTRAINTS ON THE WHOLE EIGENSPACE OF REDUCED DENSITY MATRICES

The constraints presented so far are only applied to the null spaces of RDMs. To derive the constraints covering the whole eigenspaces of RDMs, we first use the commutation relation

TABLE III. The five lowest eigenvalues of the variational and exact RDMs for the diatomic molecule LiH. The ground-state energies obtained by the two methods are $E_{\text{exact}} = -8.967\,211\,312\,701$ (E_h) and $E_{\text{var}} = -8.967\,211\,329\,766$ (E_h), respectively. The energy deviation $\Delta E = -1.707 \times 10^{-8}$ (E_h). These energies are consistent with the previous studies on this system [53,58].

	D matrix		G matrix		Q matrix	
n	Variational	Exact	Variational	Exact	Variational	Exact
1	0000 000 000 671	0000 000 001019	−0000 000 000 000	−0000 000 000 000	0000 000 000 137	0000 000 014 488 073
2	0000 000 000 920	0000 000 011 154	0000 000 000 000	0000 000 000 000	0000 001 131 230	0000 001 027 814 592
3	0000 000 004 001	0000 000 011 154	−0000 000 000 000	−0000 000 000 000	0000 001 245 966	0000 001 179 234 760
4	0000 000 004 001	0000 000 011 154	−0000 000 000 000	−0000 000 000 000	0000 001 245 966	0000 001 179 234 760
5	0000 000 007 047	0000 000 011 154	−0000 000 000 863	−0000 000 000 000	0000 001 245 966	0000 001 179 234 760

TABLE IV. The eight lowest eigenvalues of the variational and exact RDMs for random Hamiltonian 1. The Hamiltonian matrix elements in the spatial degree of freedom are randomly generated with a uniform distribution in [0,1).The ground-state energies obtained by the two methods are $E_{\text{exact}} = -5.474\,591\,092\,179$ and $E_{\text{var}} = -5.601\,757\,205\,138$, respectively. The energy deviation $\Delta E = -0.127\,166\,112\,960$.

	D matrix		*G* matrix		*Q* matrix	
n	Variational	Exact	Variational	Exact	Variational	Exact
1	0.000 000 000 000	0.000 143 928 633	−0.000 000 000 000	−0.000 000 000 000	0.000 000 000 017	0.001 790 119 018
2	0.000 613 559 566	0.001 929 013 145	−0.000 000 000 000	−0.000 000 000 000	0.000 000 000 017	0.002 205 303 031
3	0.000 613 559 566	0.001 929 013 145	−0.000 000 000 000	0.000 000 000 000	0.000 000 000 017	0.002 205 303 031
4	0.000 613 559 566	0.001 929 013 145	0.000 000 000 006	0.000 653 753 069	0.005 038 116 249	0.002 205 303 031
5	0.005 911 622 327	0.002 005 631 157	0.000 000 000 006	0.000 653 753 069	0.007 038 945 113	0.004 683 583 778
6	0.005 911 622 327	0.003 709 814 514	0.000 000 000 006	0.000 653 753 069	0.007 038 945 113	0.004 770 757 563
7	0.005 911 622 327	0.003 709 814 514	0.000 000 000 006	0.000 821 845 808	0.007 038 945 113	0.004 770 757 563
8	0.006 553 183 666	0.003 709 814 514	0.001 077 905 210	0.000 908 689 956	0.017 400 000 968	0.004 770 757 563

of two operators to have a vector equation:

$$p_1p_2|\Psi\rangle - p_2p_1|\Psi\rangle = p_3|\Psi\rangle,$$

here p_1, p_2, and p_3 are three pair operators in $\mathfrak{h}$ satisfying $p_3 = [p_1, p_2]$. Using the triangle inequality, we have

$$|p_3|\Psi\rangle| \leqslant |p_1p_2|\Psi\rangle| + |p_2p_1|\Psi\rangle|, \tag{23}$$

with $|p_1p_2|\Psi\rangle|^2 = \langle\Psi|p_2^\dagger p_1^\dagger p_1p_2|\Psi\rangle$, $|p_2p_1|\Psi\rangle|^2 = \langle\Psi|p_1^\dagger p_2^\dagger p_2p_1|\Psi\rangle$, and $|p_3|\Psi\rangle|^2 = \langle\Psi|p_3^\dagger p_3|\Psi\rangle$. To find the upper bound of $\langle\Psi|p_2^\dagger p_1^\dagger p_1p_2|\Psi\rangle$, let $|\phi\rangle = \frac{p_2|\Psi\rangle}{|p_2|\Psi\rangle|}$ and insert it into the inner product. We have

$$\begin{aligned}\langle\Psi|p_2^\dagger p_1^\dagger p_1p_2|\Psi\rangle &= \langle\Psi|p_2^\dagger|\phi\rangle\langle\phi|p_1^\dagger p_1|\phi\rangle\langle\phi|p_2|\Psi\rangle \\ &= \langle\phi|p_1^\dagger p_1|\phi\rangle\langle\Psi|p_2^\dagger|\phi\rangle\langle\phi|p_2|\Psi\rangle \\ &= \langle\phi|p_1^\dagger p_1|\phi\rangle\langle\Psi|p_2^\dagger p_2|\Psi\rangle \\ &\leqslant c_1\langle\Psi|p_2^\dagger p_2|\Psi\rangle,\end{aligned} \tag{24}$$

where $\langle\phi|p_1^\dagger p_1|\phi\rangle$ is upper-bounded by c_1. Similarly, we can have

$$\langle\Psi|p_1^\dagger p_2^\dagger p_2p_1|\Psi\rangle \leqslant c_2\langle\Psi|p_1^\dagger p_1|\Psi\rangle, \tag{25}$$

with $|\varphi\rangle = \frac{p_1|\Psi\rangle}{|p_1|\Psi\rangle|}$ and $\langle\varphi|p_2^\dagger p_2|\varphi\rangle$ upper-bounded by c_2. From Eqs. (23)–(25), we have

$$|p_3|\Psi\rangle| \leqslant c_1^{\frac{1}{2}}|p_2|\Psi\rangle| + c_2^{\frac{1}{2}}|p_1|\Psi\rangle|. \tag{26}$$

Substituting p_1 and p_2 in Eq. (26) by two eigenoperators and using the commutation relations (5a)–(6d), the constraints on the eigenspaces of 2-RMDs are given by

$$\alpha_{mn} \leqslant \left(\bar{\lambda}_N^G\right)^{\frac{1}{2}}\left[\left(\lambda_m^G\right)^{\frac{1}{2}} + \left(\lambda_n^G\right)^{\frac{1}{2}}\right], \tag{27a}$$

$$\beta_{mn} \leqslant \left(\bar{\lambda}_{N-2}^Q\right)^{\frac{1}{2}}\left(\lambda_m^D\right)^{\frac{1}{2}} + \left(\bar{\lambda}_{N+2}^D\right)^{\frac{1}{2}}\left(\lambda_n^Q\right)^{\frac{1}{2}}, \tag{27b}$$

$$\gamma_{mn} \leqslant \left(\bar{\lambda}_N^D\right)^{\frac{1}{2}}\left(\lambda_m^G\right)^{\frac{1}{2}} + \left(\bar{\lambda}_{N-2}^G\right)^{\frac{1}{2}}\left(\lambda_n^D\right)^{\frac{1}{2}}, \tag{27c}$$

and

$$\zeta_{mn} \leqslant \left(\bar{\lambda}_N^Q\right)^{\frac{1}{2}}\left(\lambda_m^G\right)^{\frac{1}{2}} + \left(\bar{\lambda}_{N+2}^G\right)^{\frac{1}{2}}\left(\lambda_n^Q\right)^{\frac{1}{2}}. \tag{27d}$$

Here $\bar{\lambda}_N^D$, $\bar{\lambda}_N^G$, and $\bar{\lambda}_N^Q$ are, respectively, the upper bounds for the eigenvalues of G, D, and Q matrices for an N-electron state. We refer the four constraints as α, β, γ, and ζ conditions. They are necessary N-representability conditions. The constraints on the null spaces, Eq. (22), are special cases of above inequalities where the eigenvalues on the right side vanish. From Eq. (26), we can see that these constraints are of geometric nature.

Figure 3 shows an example where a variational 2-RDM violates the inequality constants Eq. (27b). The system is a random-matrix Hamiltonians (Table IV). The descriptor of constraint violation is $\Delta_\beta(m,n) = \beta_{mn} - [\frac{L-N+2}{2}]^{\frac{1}{2}}(\lambda_m^D)^{\frac{1}{2}} - [\frac{N+2}{2}]^{\frac{1}{2}}(\lambda_n^Q)^{\frac{1}{2}}$, and $\Delta_\beta > 0$ indicates constraint violation. We

TABLE V. The eight lowest eigenvalues of the variational and exact RDMs for random Hamiltonian 2. The Hamiltonian matrix elements in the spatial degree of freedom are randomly generated with a uniform distribution in [0,1).The ground-state energies obtained by the two methods are $E_{\text{exact}} = -9.559\,169\,540\,991$ and $E_{\text{var}} = -9.571\,940\,687\,877$, respectively. The energy deviation $\Delta E = -0.012\,771\,146\,886$.

	D matrix		*G* matrix		*Q* matrix	
n	Variational	Exact	Variational	Exact	Variational	Exact
1	0.000 000 000 005	0.000 021 168 521	−0.000 000 000 000	−0.000 000 000 000	0.000 000 000 221	0.000 127 020 266 940
2	0.000 000 000 716	0.000 066 283 360	−0.000 000 000 000	0.000 000 000 000	0.000 700 446 139	0.000 127 020 266 941
3	0.000 000 000 716	0.000 066 283 360	−0.000 000 000 000	0.000 000 000 000	0.000 700 446 139	0.000 127 020 266 941
4	0.000 000 000 716	0.000 066 283 360	0.000 000 000 045	0.000 029 660 999	0.000 700 446 139	0.000 139 446 906 045
5	0.001 002 468 131	0.000 151 406 632	0.000 000 000 052	0.000 029 660 999	0.000 896 131 590	0.000 198 318 040 334
6	0.001 135 685 285	0.000 178 358 468	0.000 000 000 052	0.000 029 660 999	0.000 935 564 244	0.000 198 318 040 334
7	0.001 135 685 285	0.000 178 358 468	0.000 000 000 052	0.000 037 531 996	0.000 935 564 244	0.000 198 318 040 334
8	0.001 135 685 285	0.000 178 358 468	0.000 149 458 470	0.000 043 974 367	0.000 935 564 244	0.000 218 197 581 049

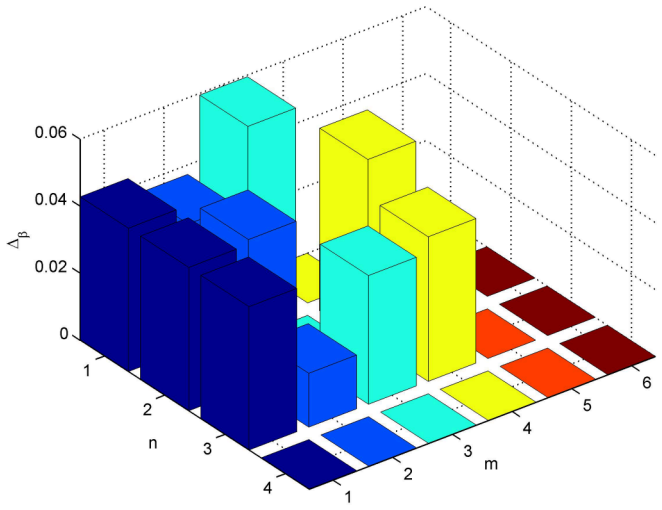

FIG. 3. An example for violation of the inequality constraints. The system is a random-matrix Hamiltonians (Table IV). Δ_β is a descriptor of constraint violation (see the definition in text). $\Delta_\beta > 0$ indicates constraint violation. m and n are the indices of the eigenvalues of D and Q, respectively. The three dark blue bars indicate the violation of the equality constraint Eq. (22) by the variational 2-RDMs. The other bars show the explicit violation of inequality constraints.

have set $\overline{\lambda}^D_{N+2} = [\frac{N+2}{2}]$ and $\overline{\lambda}^Q_{N-2} = [\frac{L-N+2}{2}]$, respectively, the universal upper bounds for the eigenvalues of D and Q matrices [73]. m and n are the indices of the eigenvalues of D and Q, respectively. As shown in Table IV, D_{var} has one null eigenvalue corresponding to $m = 1$, and Q_{var} has three corresponding to $n = 1, 2, 3$. Therefore, the three dark blue bars in Fig. 3 indicate the violation of the equality constraint Eq. (22). The other bars show the explicit violation of inequality constraints.

VI. DISCUSSION AND CONCLUSION

Even though the derivation of geometric constraints starts with a wave function in N-electron Hilbert space, these constraints are actually ensemble N-representability conditions because any mixed state can be mapped onto a pure state in a larger space (known as purification of a mixed state in quantum information) [74].

The null eigenoperators of 2-RDMs carry the information about the conserved observables of the underlying many-electron state. Equation (22) imposes restrictions on the null eigenspace of 2-RDMs to ensure the commutative compatibility of these observables. More generally, if $|\Psi\rangle$ is an eigenstate of a two-electron operator, $H = \sum_{ij,kl} K_{ij,kl} a_i^\dagger a_j^\dagger a_l a_k$, then we can generate a set of two-electron null operators by $\{[\mathfrak{n}_G, H], [\mathfrak{n}_G, [\mathfrak{n}_G, H]], \cdots\}$, which provide additional constraints on the 2-RDMs. Prediction of fractional charges and fractional spins is an indication of insufficient constraint on the conserved observables in various RDM-based electronic structure methods.

The results shown in Fig. 2(d) and for LiH suggests that, for a variational 2-RDM method, a smaller error in variational energy does not necessarily imply a smaller structural deviation of 2-RDM. The structural deviation may lead to erroneous prediction of important electronic structure properties such as the order parameters in condensed-matter physics.

Explicit violation of inequality constraints by variational 2-RDMs is not found for the Hubbard model and for LiH, which is most likely due to the insufficiency of the universal upper bounds used in our tests. The sharp upper bounds proposed by Van Neck, Johnson, and their coworkers [67,69] may be useful to enhance the inequality constraints.

Substituting an eigenoperator of 1-RDMs and an eigenoperator of 2-RDMs into Eq. (26), we can also obtain more constraints on the eigenspace of 1-RDMs and 2-RDMs. Equation (26) is general for operators defined on any Hilbert space. Therefore, the approach presented here is applicable to characterize not only N representability of fermions but also that of bosons and quantum marginal problem in general.

In this work, we derive a set of necessary N-representability conditions on 2-RDMs based on the basic geometric property of Hilbert space and the commutation relations of operators. We show that the algebra properties of the eigenoperators of 2-RDMs lead to constraints on the null spaces of 2-RDMs. Using the triangle inequality, a further analysis results in a set of inequalities expanding the constraints to the whole eigenspace of 2-RDMs. Numerical tests show that, compared with the available positive-semidefinite conditions on 2-RDMs, these conditions impose more stringent constraint on the structure of 2-RDMs.

Implementing the geometric constraints in ground-state-energy optimization will not be straightforward due to their nonlinear nature. Incorporation into SDP may be carried out in a self-consistent manner, in which these conditions provide correction to variational RDMs and new approximated constraints for the next round SDP optimization. However, this may lead to a significant increase of computational cost. Another interesting direction to explore is their application in hybrid quantum-classical computing [39,41]. Recent progresses show that N-representability conditions can be utilized to mitigate quantum error in electronic structure simulations and to reduce the number of required quantum measurements by one order.

ACKNOWLEDGMENTS

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APPENDIX: Derivation of the commutation relations for second-order reduce density matrix eigenoperators

(a) For g_m and g_n, two eigenoperators of G matrix,

$$[g_m, g_n] = \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} [v_{ij}^m a_j^\dagger a_i, v_{kl}^n a_l^\dagger a_k]$$

$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^m v_{kl}^n [a_j^\dagger a_i, a_l^\dagger a_k]$$

$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^m v_{kl}^n (a_j^\dagger a_k \delta_{il} - a_l^\dagger a_i \delta_{jk})$$

$$= \sum_{j,k,l=1}^{L} v_{lj}^{m} v_{kl}^{n} a_j^\dagger a_k - \sum_{i,k,l=1}^{L} v_{ik}^{m} v_{kl}^{n} a_l^\dagger a_i$$
$$= \sum_{i,j=1}^{L} \left[\sum_{k=1}^{L} \left(v_{kj}^{m} v_{ik}^{n} - v_{ik}^{m} v_{kj}^{n} \right) \right] a_j^\dagger a_i$$
$$= \sum_{i,j=1}^{L} \overline{v}_{ij}^{mn} a_j^\dagger a_i, \tag{A1a}$$

where

$$\overline{v}_{ij}^{mn} = \sum_{k=1}^{L} \left(v_{kj}^{m} v_{ik}^{n} - v_{ik}^{m} v_{kj}^{n} \right). \tag{A1b}$$

Now expanding $\overline{\boldsymbol{v}}^{mn}$ in the basis set $\{v_{ij}^{m'}, m' = 1, 2, \ldots, L^2\}$, we have

$$[g_m, g_n] = \sum_{m'=1}^{L^2} \sum_{i,j=1}^{L} \left(\sum_{k,l=1}^{L} \overline{v}_{kl}^{mn} v_{kl}^{m'*} \right) v_{ij}^{m'} a_j^\dagger a_i$$
$$= \sum_{m'=1}^{L^2} \Gamma_{mn}^{m'} g_{m'}, \tag{A1c}$$

where

$$\Gamma_{mn}^{m'} = \sum_{i,j=1}^{L} \overline{v}_{ij}^{mn} v_{ij}^{m'*}$$
$$= \sum_{i,j,k=1}^{L} \left(v_{kj}^{m} v_{ik}^{n} - v_{ik}^{m} v_{kj}^{n} \right) v_{ij}^{m'*}. \tag{A1d}$$

(b) For g_m and d_n, two eigenoperators of G and D matrix, respectively,

$$[g_m, d_n] = \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} \left[v_{ij}^{m} a_j^\dagger a_i, u_{kl}^{n} a_l a_k \right]$$
$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^{m} u_{kl}^{n} \left[a_j^\dagger a_i, a_l a_k \right]$$
$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^{m} u_{kl}^{n} (a_k a_i \delta_{jl} - a_l a_i \delta_{jk})$$
$$= \sum_{i,k,l=1}^{L} \left(v_{il}^{m} u_{kl}^{n} a_k a_i - v_{ik}^{m} u_{kl}^{n} a_l a_i \right)$$
$$= \sum_{i,j=1}^{L} \left[\sum_{k=1}^{L} \left(v_{ik}^{m} u_{jk}^{n} - v_{ik}^{m} u_{kj}^{n} \right) \right] a_j a_i$$
$$= \sum_{i,j=1}^{L} \overline{u}_{ij}^{mn} a_j a_i, \tag{A2a}$$

where

$$\overline{u}_{ij}^{mn} = \sum_{k=1}^{L} \left(v_{ik}^{m} u_{jk}^{n} - v_{ik}^{m} u_{kj}^{n} \right)$$
$$= -2 \sum_{k=1}^{L} v_{ik}^{m} u_{kj}^{n}. \tag{A2b}$$

Here, we have used the fact that $u_{jk}^{n} = -u_{kj}^{n}$. Now expanding $\overline{\boldsymbol{u}}^{mn}$ in the basis set $\{u_{ij}^{m'}, m' = 1, 2, \ldots, \frac{L(L-1)}{2}\}$, we have

$$[g_m, d_n] = \sum_{m'=1}^{\frac{L(L-1)}{2}} \sum_{i,j=1}^{L} \left(\sum_{k,l=1}^{L} \overline{u}_{kl}^{mn} u_{kl}^{m'*} \right) u_{ij}^{m'} a_j a_i$$
$$= \sum_{m'=1}^{\frac{L(L-1)}{2}} \Delta_{mn}^{m'} d_{m'}, \tag{A2c}$$

where

$$\Delta_{mn}^{m'} = \sum_{i,j=1}^{L} \overline{u}_{ij}^{mn} u_{ij}^{m'*}$$
$$= -2 \sum_{i,j,k=1}^{L} v_{ik}^{m} u_{kj}^{n} u_{ij}^{m'*}. \tag{A2d}$$

(c) For g_m and q_n, two eigenoperators of the G and Q matrices, respectively,

$$[g_m, q_n] = \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} \left[v_{ij}^{m} a_j^\dagger a_i, w_{kl}^{n} a_l^\dagger a_k^\dagger \right]$$
$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^{m} w_{kl}^{n} [a_j^\dagger a_i, a_l^\dagger a_k^\dagger]$$
$$= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} v_{ij}^{m} w_{kl}^{n} (a_j^\dagger a_k^\dagger \delta_{il} - a_j^\dagger a_l^\dagger \delta_{ik})$$
$$= \sum_{j,k,l=1}^{L} \left(v_{lj}^{m} w_{kl}^{n} a_j^\dagger a_k^\dagger - v_{kj}^{m} w_{kl}^{n} a_j^\dagger a_l^\dagger \right)$$
$$= \sum_{i,j=1}^{L} \left[\sum_{k=1}^{L} \left(v_{kj}^{m} w_{ik}^{n} - v_{kj}^{m} w_{ki}^{n} \right) \right] a_j^\dagger a_i^\dagger$$
$$= \sum_{i,j=1}^{L} \overline{w}_{ij}^{mn} a_j^\dagger a_i^\dagger, \tag{A3a}$$

where

$$\overline{w}_{ij}^{mn} = \sum_{k=1}^{L} \left(v_{kj}^{m} w_{ik}^{n} - v_{kj}^{m} w_{ki}^{n} \right)$$
$$= 2 \sum_{k=1}^{L} w_{ik}^{n} v_{kj}^{m}. \tag{A3b}$$

Here, we have used the fact that $w^n_{jk} = -w^n_{kj}$. Now expanding $\overline{\boldsymbol{w}}^{mn}$ in the basis set $\{w^{m'}_{ij}, m' = 1, 2, \ldots, \frac{L(L-1)}{2}\}$, we have

$$[g_m, q_n] = \sum_{m'=1}^{\frac{L(L-1)}{2}} \sum_{i,j=1}^{L} \left(\sum_{k,l=1}^{L} \overline{w}^{mn}_{kl} w^{m'*}_{kl} \right) w^{m'}_{ij} a^\dagger_j a^\dagger_i = \sum_{m'=1}^{\frac{L(L-1)}{2}} \Omega^{m'}_{mn} q_{m'}, \tag{A3c}$$

where

$$\Omega^{m'}_{mn} = \sum_{i,j=1}^{L} \overline{w}^{mn}_{ij} w^{m'*}_{ij} = 2 \sum_{i,j,k=1}^{L} w^n_{ik} v^m_{kj} w^{m'*}_{ij}. \tag{A3d}$$

(d) For q_m and d_n, two eigenoperators of the Q and D matrices, respectively,

$$\begin{aligned}
[q_m, d_n] &= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} \left[w^m_{ij} a^\dagger_j a^\dagger_i, u^n_{kl} a_l a_k \right] \\
&= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} w^m_{ij} u^n_{kl} [a^\dagger_j a^\dagger_i, a_l a_k] \\
&= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} w^m_{ij} u^n_{kl} (a^\dagger_j a_k \delta_{il} - a^\dagger_j a_l \delta_{ik} + a_k a^\dagger_i \delta_{jl} - a_l a^\dagger_i \delta_{jk}) \\
&= \sum_{i,j=1}^{L} \sum_{k,l=1}^{L} w^m_{ij} u^n_{kl} (a^\dagger_j a_k \delta_{il} - a^\dagger_j a_l \delta_{ik} - a^\dagger_i a_k \delta_{jl} + a^\dagger_i a_l \delta_{jk} + \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \\
&= \sum_{j,k,l=1}^{L} \left(w^m_{lj} u^n_{kl} a^\dagger_j a_k - w^m_{kj} u^n_{kl} a^\dagger_j a_l \right) + \sum_{i,k,l=1}^{L} \left(-w^m_{il} u^n_{kl} a^\dagger_i a_k + w^m_{ik} u^n_{kl} a^\dagger_i a_l \right) + \sum_{k,l=1}^{L} \left(w^m_{kl} u^n_{kl} - w^m_{lk} u^n_{kl} \right) \\
&= \sum_{i,j=1}^{L} \left[\sum_{k=1}^{L} \left(w^m_{kj} u^n_{ik} - w^m_{lj} u^n_{ki} - w^m_{jk} u^n_{ik} + w^m_{jk} u^n_{ki} \right) \right] a^\dagger_j a_i + \sum_{k,l=1}^{L} \left(w^m_{kl} u^n_{kl} - w^m_{lk} u^n_{kl} \right) \\
&= \sum_{i,j=1}^{L} \left[\sum_{k=1}^{L} \left(w^m_{kj} u^n_{ik} - w^m_{kj} u^n_{ki} - w^m_{jk} u^n_{ik} + w^m_{jk} u^n_{ki} \right) + \frac{1}{N} \sum_{k,l=1}^{L} \left(w^m_{kl} u^n_{kl} - w^m_{lk} u^n_{kl} \right) \delta_{ij} \right] a^\dagger_j a_i \\
&= \sum_{i,j=1}^{L} \overline{v}^{mn}_{ij} a^\dagger_j a_i,
\end{aligned} \tag{A4a}$$

where we have restricted ourselves to N-electron Hilbert space, and

$$\begin{aligned}
\overline{v}^{mn}_{ij} &= \sum_{k=1}^{L} \left(w^m_{kj} u^n_{ik} - w^m_{kj} u^n_{ki} - w^m_{jk} u^n_{ik} + w^m_{jk} u^n_{ki} \right) + \frac{1}{N} \sum_{k,l=1}^{L} \left(w^m_{kl} u^n_{kl} - w^m_{lk} u^n_{kl} \right) \\
&= 4 \left(\sum_{k=1}^{L} u^n_{ik} w^m_{kj} - \frac{1}{2N} \delta_{ij} \sum_{k,l=1}^{L} u^n_{lk} w^m_{kl} \right).
\end{aligned} \tag{A4b}$$

Here, we have used the fact that $u^n_{jk} = -u^n_{kj}$ and $w^n_{jk} = -w^n_{kj}$. Now expanding $\overline{\boldsymbol{v}}^{mn}$ in the basis set $\{v^{m'}_{ij}, m' = 1, 2, \ldots, L^2\}$, we have

$$\begin{aligned}
[q_m, d_n] &= 4 \sum_{m'=1}^{L^2} \sum_{i,j=1}^{L} \left(\sum_{k=1}^{L} u^n_{ik} w^m_{kj} - \frac{1}{2N} \delta_{ij} \sum_{k,l=1}^{L} u^n_{lk} w^m_{kl} \right) v^{m'}_{ij} a^\dagger_j a_i \\
&= \sum_{m'=1}^{L^2} \Theta^{m'}_{mn} g_{m'},
\end{aligned} \tag{A4c}$$

where

$$\begin{aligned}
\Omega^{m'}_{mn} &= \sum_{i,j=1}^{L} \overline{v}^{mn}_{ij} v^{m'*}_{ij} \\
&= 4 \sum_{i,j,k=1}^{L} \left(u^n_{ik} w^m_{kj} - \frac{1}{2N} \delta_{ij} \sum_{l=1}^{L} u^n_{lk} w^m_{kl} \right) v^{m'*}_{ij} \\
&= 4 \sum_{i,j,k=1}^{L} \left(u^n_{ik} w^m_{kj} v^{m'*}_{ij} - \frac{1}{2N} u^n_{ij} w^m_{ji} v^{m'*}_{kk} \right).
\end{aligned} \tag{A4d}$$

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