Large eigenvalue of the cumulant part of the two-electron reduced density matrix as a measure of off-diagonal long-range order

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Off-diagonal long-range order (ODLRO) in the two-electron reduced density matrix (2-RDM) has long been recognized as a mathematical characteristic of conventional superconductors. The large eigenvalue of the 2-RDM has been shown to be a useful measure of this long-range order. The 2-RDM can be represented as the sum of a connected (cumulant) piece and an unconnected piece. In this work, we show that the cumulant 2-RDM also has a large eigenvalue in the limit of ODLRO. The largest eigenvalue of the cumulant 2-RDM, we prove, is bounded from above by N. In the limit of extreme pairing, such as Cooper pairing, the largest eigenvalue and the trace of the cumulant 2-RDM approach their extreme values of N and $-N$, respectively. While the trace of the cumulant 2-RDM, which is computable from only a knowledge of the 1-RDM, can reflect ODLRO, it alone does not appear to be a sufficient criterion. The large eigenvalue of the cumulant 2-RDM, we show, implies the large eigenvalue of the 2-RDM and, hence, is a natural measure of ODLRO that vanishes in the mean-field limit.

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I. INTRODUCTION

Superconductivity is an important phenomenon in condensed-matter physics arising from a pairing of the electrons that exhibits long-range order [1–3]. Both Yang [4] and Sasaki [5,6] showed that this long-range order, called off-diagonal long-range order (ODLRO) by Yang, is associated with a large eigenvalue in the two-electron reduced density matrix (2-RDM). Unlike bosonic long-range order, which is characterized by a large eigenvalue in the one-electron reduced density matrix (1-RDM), fermionic ODLRO has no classical analog, since the off-diagonal elements of the 2-RDM are nonzero only in the quantum description. Coleman [7,8] showed that the large eigenvalue of the 2-RDM occurs for finite N-electron systems in the context of N-projected Bardeen-Cooper-Schrieffer (BCS) or antisymmetric geminal power (AGP) wave functions. As a result, the magnitude of the large eigenvalue of the 2-RDM can be used as an indicator of phenomena with ODLRO including superconductivity [9–11].

Because electrons are indistinguishable with pairwise interactions, the total energy of any molecule or material is a linear functional of the 2-RDM [8,12]. In general, the 2-RDM provides information concerning pair properties of a fermionic system. Diagonal elements give information about the populations of fermion pairs, while off-diagonal elements give information about the correlations between fermion pairs. By unitary transformation, we can obtain the pair probabilities with respect to different sets of orbitals including points in coordinate space. Furthermore, the 2-RDM contains the probability distributions for not only two fermion particles but also one fermion particle and one fermion hole as well as two fermion holes [8,12,13]. Recent work [14] has proposed that the many-body correlations contained in the 2-RDM are accessible by ultrafast pump-probe experiments, as the probability of a system remaining in the ground state when perturbed in this manner is expressible in terms of the 2-RDM or its connected (cumulant) part.

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Cumulants, which were first discussed by Thiele [15] in the 1800s and connected across different areas of physics by Kubo in the 1960s [16], are widely applied in both quantum field theory [17–19] and quantum chemistry [12,20,21]. The cumulant expansions of reduced density matrices (RDMs) have been particularly useful in electronic structure where they have been used to remove the indeterminacy of the contracted Schrödinger equation [22–27]. The cumulant 2-RDM has been previously studied as a quantifier of electron correlation and entanglement in both time-independent [14,28–31] and time-dependent systems [32]. In this paper we examine the cumulant part of the 2-RDM as a measure of ODLRO, which is a special type of correlation and entanglement. While the full 2-RDM scales quadratically with system size, the cumulant 2-RDM scales linearly with system size, making it more appropriate for the study of the extent of ODLRO in finite systems. We show that like the 2-RDM the cumulant part of the 2-RDM also exhibits a large positive eigenvalue in the presence of long-range order. Furthermore, in the limit that the size (rank) of the one-electron basis set approaches infinity, we also find that the largest eigenvalue of the cumulant 2-RDM shares with the largest eigenvalue of the 2-RDM the same upper bound of N. We also find that the trace of the cumulant 2-RDM can reach its extreme value of $-N$ in the presence of ODLRO even though this limiting behavior does not appear to be exclusively associated with ODLRO [33,34].

II. THEORY

The ensemble N-particle density matrix $D(123\ldots N;\bar{1}\bar{2}\bar{3}\ldots\bar{N})$ can be expressed in terms of a set of N-particle wave functions $\{\Psi_i(123\ldots N)\}$ and non-negative weights $\{w_i\}$:

$$D(123\ldots N;\bar{1}\bar{2}\bar{3}\ldots\bar{N}) = \sum_i w_i \Psi_i(123\ldots N)\Psi_i^*(\bar{1}\bar{2}\bar{3}\ldots\bar{N}), \quad (1)$$

where the roman numbers represent the spatial and spin coordinates of each particle. Integrating the N-particle density matrix over all particles save two yields the 2-RDM

$$^{2}D(1,2;\bar{1},\bar{2}) = \int D(123\ldots N;\bar{1}\bar{2}3\ldots N)d3\ldots dN. \quad (2)$$

Importantly, the coordinates of the 2-RDM can be expanded in terms of a set of one-particle functions (spin orbitals) $\{\phi_i(1)\}$:

$$^{2}D(12;\bar{1}\bar{2}) = \sum_{i,j,k,l} {}^{2}D^{ij}_{kl}\phi_i(1)\phi_j(2)\phi^*_k(\bar{1})\phi^*_l(\bar{2}), \quad (3)$$

where ${}^{2}D^{ij}_{kl}$ are the elements of the 2-RDM. Consider the cumulant expansion of the 2-RDM,

$${}^{2}D^{ij}_{kl} = 2\,{}^{1}D^{i}_{k} \wedge {}^{1}D^{j}_{l} + {}^{2}\Delta^{ij}_{kl}, \quad (4)$$

where the Grassmann wedge product [20,35,36] is an antisymmetric tensor product,

$$2\,{}^{1}D^{i}_{k} \wedge {}^{1}D^{j}_{l} = {}^{1}D^{i}_{k}\,{}^{1}D^{j}_{l} - {}^{1}D^{i}_{l}\,{}^{1}D^{j}_{k}. \quad (5)$$

The cumulant (or connected) part of the 2-RDM cannot be written as a wedge product of lower RDMs. We normalize the 2-RDM to have a trace of $N(N-1)$. With these definitions we consider three theorems and two corollaries regarding the large eigenvalue and the trace of the cumulant 2-RDM.

Both Yang [4] and Sasaki [5] showed that the 2-RDM can have an eigenvalue (geminal occupation number) as large as the number N of electrons in the system which is a signature of ODLRO. This maximum occupation occurs for ODLRO in a one-electron basis set of infinite size. Yang and Sasaki's result can be extended to show that the cumulant 2-RDM can have a large eigenvalue, also bounded by N.

Theorem 1. The largest eigenvalue of the cumulant 2-RDM is bounded by N.

Proof. Consider the eigenvector v associated with the largest eigenvalue of the 2-RDM where the number of one-electron basis functions, also known as the rank of the basis set, equals r. Yang [4] and Sasaki [5] showed that

$$\lambda_D = v^{\dagger}\,{}^{2}D\,v \leqslant N. \quad (6)$$

It can be shown that the cumulant 2-RDM has the following eigenvalue bound:

$$\begin{aligned}
\lambda_\Delta &= v^{\dagger}\,{}^{2}\Delta\,v, && (7)\\
&= v^{\dagger}\,({}^{2}D - 2\,{}^{1}D \wedge {}^{1}D)\,v && (8)\\
&= v^{\dagger}\,{}^{2}D\,v - 2v^{\dagger}({}^{1}D \wedge {}^{1}D)v && (9)\\
&= \lambda_D - 2v^{\dagger}({}^{1}D \wedge {}^{1}D)v && (10)\\
&\leqslant \lambda_D && (11)\\
&\leqslant N, && (12)
\end{aligned}$$

where we have employed the positive semidefiniteness of ${}^{1}D \wedge {}^{1}D$, that is,

$$v^{\dagger}({}^{1}D \wedge {}^{1}D)v \geqslant 0, \quad (13)$$

for all v.

Pairing wave functions, known as extreme AGP [6–8] or projected BCS wave functions, that exhibit a large eigenvalue in the 2-RDM also exhibit a large eigenvalue in the cumulant part of the 2-RDM that is indicative of long-range order.

Theorem 2. For the extreme AGP wave function, the eigenvalue λ_D of the 2-RDM and the eigenvalue λ_Δ of its cumulant are related as follows:

$$\lambda_\Delta = \lambda_D - \frac{N^2}{r^2}.$$

Proof. When the 2-RDM and its cumulant are from an extreme AGP wave function, the 1-RDM is a scalar multiple of the identity matrix with a scalar factor equal to the number of electrons divided by the rank N/r:

$${}^{1}D = \frac{N}{r}\,{}^{1}I. \quad (14)$$

Therefore, for the extreme AGP wave function, we have

$$\lambda_\Delta = \lambda_D - 2\frac{N^2}{r^2}v^{\dagger}({}^{1}I \wedge {}^{1}I)v, \quad (15)$$

$$\lambda_\Delta = \lambda_D - \frac{N^2}{r^2}. \quad (16)$$

Corollary 1. In the limit that the size of the one-electron basis set approaches infinity, the 2-RDM and the cumulant 2-RDM from an extreme AGP wave function share the same large eigenvalue equal to N.

Proof. The corollary follows immediately from Theorem 2 and Yang and Sasaki's [4,5] theorem. The contribution of the unconnected part of the 2-RDM to the large eigenvalue of either the 2-RDM or its cumulant part vanishes in the limit that the rank r (or size) of the one-electron basis set approaches infinity.

The large eigenvalue in the cumulant (connected) 2-RDM occurs if the order of the system extends over N electrons, which we refer to as long-range order. Because the cumulant part of the 2-RDM is connected, it scales linearly with the size of the system, and hence its largest eigenvalue cannot scale faster than linear in the number of N electrons.

Even though the trace of the cumulant 2-RDM is computable from only a knowledge of the 1-RDM (in fact, just the 1-RDM's eigenvalues), it can reflect the emergence of ODLRO in the 2-RDM.

Theorem 3. The trace of the cumulant 2-RDM becomes increasingly negative with the emergence of long-range order. The trace of the cumulant 2-RDM is always nonpositive with a lower bound of $-N$,

$$-N \leqslant \mathrm{Tr}({}^{2}\Delta) \leqslant 0;$$

in the mean-field limit the trace of the cumulant 2-RDM is 0,

$$\mathrm{Tr}({}^{2}\Delta_{\mathrm{mf}}) = 0;$$

and in the extreme-AGP limit the trace of the cumulant 2-RDM is

$$\mathrm{Tr}({}^{2}\Delta_{\mathrm{ext}}) = -N\left(1 - \frac{N}{r}\right).$$

Proof. In general,

$$\mathrm{Tr}({}^{2}\Delta) = \mathrm{Tr}\big({}^{2}D^{ij}_{kl}\big) - 2\,\mathrm{Tr}\big({}^{1}D^{i}_{k} \wedge {}^{1}D^{j}_{l}\big), \quad (17)$$

$$\mathrm{Tr}({}^{2}\Delta) = \mathrm{Tr}({}^{1}D^{2}) - N. \quad (18)$$

Because the eigenvalues of the 1-RDM lie between 0 and 1, we have

$$0 \leqslant \mathrm{Tr}[{}^1D(1 - {}^1D)], \tag{19}$$

$$\mathrm{Tr}({}^1D^2) \leqslant \mathrm{Tr}({}^1D), \tag{20}$$

$$\mathrm{Tr}({}^1D^2) \leqslant N. \tag{21}$$

Furthermore, the trace of the 1-RDM squared is non-negative:

$$\mathrm{Tr}({}^1D^2) \geqslant 0. \tag{22}$$

Combining Eq. (18) with Eqs. (21) and (22) proves that the trace of the cumulant 2-RDM has a lower bound of $-N$ and an upper bound of 0. Because the trace of the 1-RDM squared can be written as the sum of the 1-RDM's eigenvalues, the trace of the cumulant 2-RDM can also be expressed in terms of the 1-RDM's eigenvalues n_i:

$$\mathrm{Tr}({}^2\Delta) = \sum_i n_i^2 - N. \tag{23}$$

In the mean-field limit the trace of the cumulant 2-RDM is 0 because the cumulant 2-RDM itself vanishes since the electrons (orbitals) are not correlated; that is, they are not statistically dependent. For the extreme AGP wave function, the trace of the cumulant is given by

$$\mathrm{Tr}({}^2\Delta_{\mathrm{ext}}) = N(N-1) - 2\frac{N^2}{r^2}\mathrm{Tr}\left({}^1I_k^i \wedge {}^1I_l^j\right), \tag{24}$$

$$\mathrm{Tr}({}^2\Delta_{\mathrm{ext}}) = N(N-1) - \frac{N^2}{r^2}r(r-1), \tag{25}$$

$$\mathrm{Tr}({}^2\Delta_{\mathrm{ext}}) = -N\left(1 - \frac{N}{r}\right). \tag{26}$$

Corollary 2. In the limit that the size of the one-electron basis set approaches infinity, the trace of the cumulant 2-RDM from an extreme AGP wave function approaches $-N$

Proof. In the limit that the rank r approaches infinity, it follows from Theorem 3 that the trace of the cumulant approaches $-N$.

III. APPLICATIONS

We explore the large eigenvalue in the cumulant part of the 2-RDM by considering the family of Hamiltonian operators [8],

$$\hat{H} = N - (N-2)\sum_i \eta_i (a_{i\alpha}^\dagger a_{i\alpha} + a_{i\beta}^\dagger a_{i\beta}) - \sum_{ij} \xi_i \xi_j^* a_{i\alpha}^\dagger a_{i\beta}^\dagger a_{j\beta} a_{j\alpha}, \tag{27}$$

where the η_i are defined in terms of the ξ_i,

$$\eta_i = |\xi_i|^2, \tag{28}$$

and the ξ_i are the expansion coefficients in the two-electron function (geminal) $g(12)$,

$$g(12) = 2\sum_i \xi_i \phi_{i\alpha}(1) \wedge \phi_{i\beta}(2). \tag{29}$$

For even N each Hamiltonian in the family has a unique N-electron ground-state AGP wave function,

$$\Psi(123\ldots N) = g(12) \wedge g(34) \wedge \ldots \wedge g[(N-1)N], \tag{30}$$

that is generated from wedge products of the geminal $g(12)$. When all of the η_i equal 1, the ground-state solution is an extreme AGP wave function with maximum ODLRO.

Varying the geminal's expansion coefficients in the above Hamiltonian allows us to examine the onset of pairing and long-range order in a quantum system through the large eigenvalues of both the 2-RDM and its cumulant part. We approximate the mean-field case using a geminal in which $N/2$ of the $\eta_{i,\mathrm{mf}}$ values approach 1 and $N/2$ approach 0. The extreme case has all of the $\eta_{i,\mathrm{ext}}$ equal to 1. We tune between the mean-field case and the extreme case using an expression for η_i of the form

$$\eta_i = \alpha\eta_{i,\mathrm{ext}} + (1-\alpha)\eta_{i,\mathrm{mf}}, \tag{31}$$

where α is a real value between 0 and 1. When α is set to 0, we create a pure mean-field geminal, while setting it to 1 creates an extreme AGP wave function, allowing us to show how the large eigenvalue detects long-range order by tuning α between these two values.

The maximum possible eigenvalue λ_Δ ($=N$) of the cumulant 2-RDM occurs when the rank r of the one-electron basis set approaches infinity. In a finite basis set with rank r the maximum λ_Δ, strictly less than N, occurs at half filling when $N = r/2$. When $N < r/2$, there are not enough particles to support the ODLRO at half filling, and when $N > r/2$, there are not enough holes to support the ODLRO at half filling. In the following examples, to make comparisons of the large eigenvalues and traces of the 2-RDM and its cumulant part in a finite basis set, we use half filling to maximize the possible ODLRO.

As a general quantum system of 50 electrons in 100 orbitals is modulated between a mean-field geminal and an extreme AGP wave function, the large eigenvalue λ_Δ of both the 2-RDM and its cumulant increase sharply with the initial onset of long-range order and begin to plateau when α is approximately 0.3. While only the large eigenvalue λ_Δ of the cumulant is shown in Fig. 1, the large eigenvalue λ_D of the full 2-RDM follows essentially the same curve, its values slightly above those of λ_Δ. As α approaches 1, the large eigenvalues gradually approach their maximum. The largest eigenvalue λ_Δ can detect even a small amount of long-range order and thereby measure the difference between an extreme AGP system and a nonextreme AGP system, even a nonextreme AGP system with some degree of long-range order. As the system is tuned from a mean-field case to an extreme AGP system, the difference between the large eigenvalue of the 2-RDM and its cumulant is reduced from a relatively large value to a smaller, limiting value. For an extreme AGP system where $N = r/2$, the large eigenvalue of the cumulant part λ_Δ is exactly less than the large eigenvalue λ_D of the 2-RDM by 1/4:

$$\lambda_\Delta = \lambda_D - \tfrac{1}{4}. \tag{32}$$

In addition to the large eigenvalues λ_D and λ_Δ, the increases of this difference $\lambda_\Delta - \lambda_D$ can also be a useful measure of ODLRO with the difference being -1 in the mean-field limit in the absence of ODLRO.

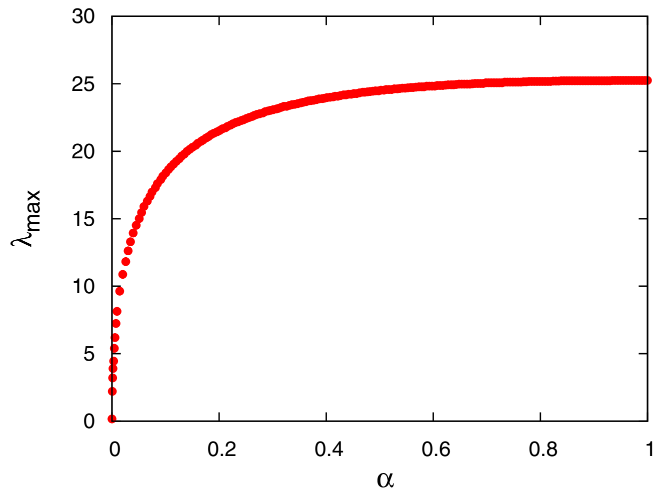

FIG. 1. (Color online) The largest eigenvalue of the cumulant part of the 2-RDM is given as a function of α, the tuning parameter, for a general 50-electron, 100-orbital quantum system. As α increases, the eigenvalue captures the emergence of ODLRO.

In addition to the large eigenvalue of the cumulant 2-RDM, we show in Table I, for a general quantum system of 50 electrons, that the trace of the cumulant can also reflect the presence of long-range order. Unlike the trace of the 2-RDM, which is constant for a given system of N electrons, the trace of the cumulant decreases with the onset of long-range order, as the geminal is tuned between a mean-field case and an extreme AGP wave function, reaching a minimum value when α is equal to 1. For an extreme AGP wave function when $N = r/2$, the trace of the cumulant part is equal to

$$\mathrm{Tr}(^2\Delta) = \tfrac{1}{2} - \lambda_D. \tag{33}$$

The absolute value of the trace follows the same trend as the large eigenvalue of the 2-RDM and the large eigenvalue of the cumulant.

IV. DISCUSSION AND CONCLUSIONS

The largest eigenvalue of the cumulant 2-RDM was shown to provide effective measures of ODLRO in quantum many-fermion systems. While Yang [4] and Sasaki [5] previously proved that the largest eigenvalue of the 2-RDM approaches an upper bound of N in the limit of maximum ODLRO, we proved that the largest eigenvalue of the cumulant 2-RDM (i) implies the large eigenvalue of the 2-RDM and (ii) approaches the same upper bound of N. Unlike the largest eigenvalue of the 2-RDM, the largest eigenvalue of the cumulant 2-RDM vanishes in the absence of ODLRO in the mean-field limit [37]. Furthermore, while the 2-RDM has a fixed trace for any system with a fixed number of particles, the variable trace of the cumulant 2-RDM can also reflect the emergence of long-range order. For an extreme AGP wave function in the infinite basis-set limit, the trace of the cumulant 2-RDM reaches its lower bound of $-N$ and thereby reveals maximum ODLRO. While the large eigenvalue of the cumulant 2-RDM implies the large eigenvalue of the 2-RDM, it is also important to note that the trace of the cumulant 2-RDM can also reach its extreme $-N$ value in cases that are not typically associated with ODLRO (see, for example, recent calculations on pairing Hamiltonians [11] and the harmonium model [38,39]).

Since the development of density functional theory [40], there has been significant interest in how much information is contained within the 1-RDM. The 1-RDM contains significant information about a quantum system's correlation, entanglement, and openness. Recently, a formally complete set of pure N-representability conditions for the 1-RDM, also known as generalized Pauli conditions, have been derived [41,42] and studied computationally in atoms and molecules [43–47]. The proximity of the 1-RDM to the boundary of its pure N-representable set, or its quasipinning to the boundary, is conjectured to place significant restrictions on the correlation and complexity of the wave function. Chakraborty and one of the authors (D.A.M.) [48] have also recently shown that the violation of these conditions by the 1-RDM provides a sufficient condition for the openness of an N-fermion quantum system. In this paper we found that through the trace of the cumulant 2-RDM, which depends quadratically upon the 1-RDM, the 1-RDM contains an imprint of ODLRO. This result may be useful in improving 1-RDM-based (or geminal-based) energy functionals in electronic structure theory [49–52]. As recent work [53] has experimentally determined the 1-RDM for ultracold fermionic atoms in a double-well potential, the examination of the 1-RDM with respect to ODLRO has the potential to be applied to experimental systems.

Molecules and materials have a plethora of possible energies and properties from the arrangement of atoms in chemical bonds. Special arrangements such as copper-oxide planes have been shown to exhibit extraordinary properties such as high-temperature superconductivity [54]. Recent work [55] suggests that ODLRO arises in cuprate and iron-based high-temperature superconductors as a result of short-range Coulomb repulsion and long-range attraction between electron pairs in alternating lattice structures. Pairing phenomena in ultracold fermi gases [56], especially in the BCS–BEC (Bose-Einstein condensate) limit, are of experimental interest [57–60] as a method of explaining high-temperature superconductivity. The large eigenvalue of the cumulant 2-RDM provides a useful quantity for both quantifying and understanding the presence of ODLRO in quantum molecular systems. While the present results are directly applicable to theoretical and computational studies of long-range order in phenomena

TABLE I. Relationships among the large eigenvalue λ_D of the 2-RDM, the large eigenvalue λ_Δ of the cumulant 2-RDM, and the trace of the cumulant 2-RDM are shown as functions of the tuning parameter α for a 50-electron, 100-orbital quantum system. As α increases, all three quantities capture the emergence of ODLRO. The cumulant-derived quantities also vanish in the mean-field limit in the absence of ODLRO.

α	λ_D	λ_Δ	$\mathrm{Tr}(^1D)$	$\mathrm{Tr}(^2D)$	$\mathrm{Tr}(^2\Delta)$
0.0	1.00	0.00	50	4950	0.00
0.1	18.69	18.37	50	4950	−18.12
0.2	21.82	21.53	50	4950	−21.28
0.5	24.76	24.50	50	4950	−24.25
1.0	25.50	25.25	50	4950	−25.00

like superconductivity, they are also applicable to the study of more general materials with long-range order behavior. Copper oxide compounds, for example, have a high-temperature state referred to as a pseudogap metal which has both simple metallic character and long-range quantum entanglement [61]. The model Hamiltonians studied in this paper show that a continuous curve of largest cumulant 2-RDM eigenvalues can be generated in the range from 0 to N, with 0 being the mean-field limit and N being the extreme AGP (superconducting) limit. Similarly, materials can have large cumulant 2-RDM eigenvalues that indicate a degree of long-range order between that of a typical insulating material and that of a superconductor. The indicators for ODLRO, developed here, provide tools for exploring more fully the spectrum of quantum long-range order in molecular systems and materials.

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