Entangling and disentangling many-electron quantum systems with an electric field

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We show that the electron correlation of a molecular system can be enhanced or diminished through the application of a homogeneous electric field antiparallel or parallel to the system's intrinsic dipole moment. More generally, we prove that any external stimulus that significantly changes the expectation value of a oneelectron operator with nondegenerate minimum and maximum eigenvalues can be used to control the degree of a molecule's electron correlation. Computationally, the effect is demonstrated in HeH⁺, MgH⁺, BH, HCN, H₂O, HF, formaldehyde, and a fluorescent dye. Furthermore, we show in calculations with an array of formaldehyde (CH₂O) molecules that the field can control not only the electron correlation of a single formaldehyde molecule but also the entanglement among formaldehyde molecules. The quantum control of correlation and entanglement has potential applications in the design of molecules with tunable properties and the stabilization of qubits in quantum computations.

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I. INTRODUCTION

The expectation values of two or more subsystems of a purestate quantum system can become inseparable in a process known as entanglement. Formally, entanglement is present between two subsystems of a pure-state quantum system when the system's density matrix cannot be expressed as a product of the subsystems' density matrices [1,2]. In a many-electron quantum system there is a special type of entanglement known as electron correlation which occurs when the pure-state manyelectron density matrix cannot be expressed as the product of one-electron density matrices [3-5]. In addition to the computation of electron correlation, a significant challenge in quantum theory is the control of a molecule's electron correlation [6-9]. In this paper we show that the degree of electron correlation and entanglement in quantum molecular systems can be controlled through an external stimulus such as an electric field.

Computationally, we show the application of an electric field in the direction parallel to a molecule's dipole moment decreases the degree of electron correlation in the molecule, and conversely, the application of an electric field in the direction opposite to a molecule's dipole moment increases the degree of electron correlation in the molecule. More generally, using the set of one-electron reduced density matrices (1-RDMs) and notions of convexity, we prove mathematically that any external stimulus that significantly changes the expectation value of a one-electron operator with nondegenerate minimum and maximum eigenvalues can be used to control the degree of electron correlation in the molecule. The concept is illustrated through calculations with the molecules HeH⁺, MgH⁺, BH, HCN, H₂O, HF, CH₂O, and a fluorescent dye. Furthermore, we show in calculations with formaldehyde (CH₂O) that the field can control not only the electron correlation of a formaldehyde

II. THEORY

An electric field applied to a molecular system, whose magnitude provides a continuous parameter for controlling the strength of the dipole moment, can be employed to control the degree of the molecule's electron correlation. More generally, we can show that any adjustable external stimulus that changes the expectation value of a one-electron operator ${}^{1}\hat{O}$ with nondegenerate minimum and maximum eigenvalues can be employed to control a molecule's electron correlation. To demonstrate this result, we will rely upon some key ideas from convexity and reduced-density-matrix theory [10–12].

The 1-RDM of a pure *N*-electron state is computable from the state's *N*-electron wave function

$${}^{1}D(1,\bar{1}) = N \int \psi(123,\dots,N)\psi^{*}(\bar{1}23,\dots,N) \times d(23,\dots,N).$$
(1)

Such a 1-RDM is said to be *pure N-representable* [13–17]. Although the set of pure *N*-representable 1-RDMs is not convex, it is contained within the convex set of ensemble *N*-representable 1-RDMs [14]. A 1-RDM is *ensemble N*-representable if and only if it can be obtained from the integration of at least one ensemble *N*-electron density matrix [10,11,13]. Because the set is convex, all 1-RDMs within the set can be expressed as convex combinations of its extreme 1-RDMs [12]. Coleman proved the key result that the extreme 1-RDMs are the pure-state 1-RDMs whose wave functions are Slater determinants [11,13]. Formally, the convex set of ensemble *N*-representable 1-RDMs is the *convex hull* of its extreme

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molecule but also the entanglement among formaldehyde molecules in an array. The control of a molecule's correlation and entanglement has potential applications to designing molecules and materials with controllable properties as well as modifying the degree of correlation between fundamental units such as qubits in quantum computation.

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elements, $P_N^1 = \text{Conv}(S_{\text{Slater}})$ where S_{Slater} is the set of 1-RDMs whose *N*-electron pre-images are Slater determinants.

The expectation value of the one-electron operator ${}^{1}\hat{O}$ is expressible in terms of the 1-RDM:

$$\langle {}^{1}\hat{O}\rangle(\epsilon) = \operatorname{Tr}[{}^{1}\hat{O} {}^{1}D(\epsilon)],$$
 (2)

where ϵ is a controllable parameter such as an electric field for controlling the expectation value of \hat{O} . The ϵ controls the expectation value of \hat{O} by changing ${}^{1}D(\epsilon)$ which is the 1-RDM of the ground state of the system with the stimulus ϵ . By convexity the minimum and maximum expectation values occur at one or more extreme 1-RDMs. Importantly, from Coleman's theorem [13] we know that these 1-RDMs are contained in S_{Slater} , the set of uncorrelated 1-RDMs. From these two observations we obtain the following theorem.

Theorem. If the operator ${}^{1}\hat{O}$ has a nondegenerate ground state, then there is a unique extreme 1-RDM in the uncorrelated set S_{Slater} for which the minimum expectation value of ${}^{1}\hat{O}$ is achieved.

Proof. Because the expectation value of a one-electron observable is an affine function of the 1-RDM, the minimization of the expectation value over the convex set of 1-RDMs P_N^1 must occur at one or more extreme points. Because the operator ${}^1\hat{O}$ is assumed to have a nondegenerate ground state, the minimum must occur at a unique point. By Coleman's theorem the unique extreme point at which the minimum occurs must be a 1-RDM with a Slater-determinant pre-image, that is a 1-RDM in the uncorrelated set S_{Slater} .

Similarly, if the operator ${}^{1}\hat{O}$ has a nondegenerate maximal state, then there is a unique extreme 1-RDM in the uncorrelated set S_{Slater} for which the maximum expectation value of ${}^{1}\hat{O}$ is achieved. Consequently, the expectation value of the operator ${}^{1}\hat{O}$ can be controlled with ϵ to steer the 1-RDM towards the uncorrelated extreme 1-RDM at which the expectation value reaches its minimum or maximum value.

Controllable 1-electron observables that correspond to nondegenerate 1-electron operators provide a general mechanism through their response to an external stimulus such as an electric field for modulating the electron correlation of a molecular system. In the case of the dipole moment, as the electric dipole moment is moved towards an extreme by the electric field, the 1-RDM moves toward the extreme 1-RDM corresponding to the Slater determinant with the minimum or maximum observable. Typically, a molecule with a greater polarizability will be more sensitive to the electric field, and hence, will exhibit greater changes in its electron correlation. Practically, the magnitude of the stimulus must be less than the value required to change the electronic identity of the molecule; in the case of the electric-field stimulus the field must be less than the value required to ionize the molecule. Figure 1 shows a schematic representation of the convex set of 1-RDMs. The color scheme of the set is chosen to represent its convexity with the most blue color (minimum value) and its yellow color (maximum value) occurring at extreme points (extreme 1-RDMs) of the set. Changing the electric field steers the 1-RDM, represented by the dot, towards increasing or decreasing the dipole moment. In the direction towards the boundary of the set of 1-RDMs, the electric field decreases the



FIG. 1. A schematic representation of the convex set of 1-RDMs is depicted. The color scheme of the set is chosen to represent its convexity with the most blue color (minimum value) and its most yellow color (maximum value) occurring at extreme points (extreme 1-RDMs) of the set. Changing the electric field steers the 1-RDM, represented by the dot, towards increasing or decreasing the dipole moment. In the direction towards the boundary of the set of 1-RDMs, the electric field decreases the electron correlation while in the opposite direction, the electric field increases the electron correlation.

electron correlation while in the opposite direction, the electric field increases the electron correlation.

III. APPLICATIONS

After a discussion of computational methodology, we explore computationally the entangling and disentangling of molecules with an electric field through computations with two-electron systems HeH⁺ and MgH⁺ where only the two valence electrons of MgH⁺ are correlated; molecules BH, HCN, H₂O, and HF; the formaldehyde molecule CH₂O; and an array of six formaldehyde molecules CH₂O, as well as a fluorescent dye mimic of VF2.1.H.

A. Computational methodology

Molecular electronic structure calculations were performed on HeH⁺, MgH⁺, BH, HCN, H₂O, HF, formaldehyde, formaldehyde clusters, and a fluorescent dye. The two-electron calculation of HeH⁺ was performed with full configuration interaction (FCI), and the calculation of MgH⁺ was performed with a complete active-space configuration interaction (CASCI) using an active space of 2 electrons in 31 orbitals. For the larger molecules we employed the parametric twoelectron reduced density matrix (2-RDM) method in which a parametrization of the 2-RDM is directly computed without the many-electron wave function [18-25]. The augmented correlation-consistent polarized valence double-zeta (aug-ccpVDZ) basis set was employed for calculations of HeH⁺, MgH^+ , BH, HCN, H_2O , and HF, the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set was employed for calculations of formaldehyde and the formaldehydecluster [26,27], and the Dunning-Hay double-zeta basis set was employed for the dye mimic [28].

The degree of electron correlation in the 1-RDM is quantified through the von Neumann entropy [29], equivalent to its first-order Rényi entropy [30],

$$S_1 = -\text{Tr}[{}^1D\ln({}^1D)]$$
(3)

or its second-order Rényi entropy [30-32].

$$S_2 = -\ln[\mathrm{Tr}(^1 D^2)]. \tag{4}$$

As in Eq. (1), the 1-RDM is normalized to N. With this normalization the von Neumann entropy of the 1-RDM is a nonnegative quantity than vanishes only in the absence of electron correlation. While the 1-RDM can also be normalized to 1 in the definition of entropy, such a normalization produces an entropy that is not zero in the absence of electron correlation and that is not size-consistent upon the doubling of the quantum system. Note that electron correlation, a form of entanglement, is not the same as the electron correlation energy, and that the relationship between these two quantities is nontrivial [4,33,34]. Refer to Appendix A for a discussion of electron correlation in terms of entanglement and Appendix B for additional details and references on the use of von Neumann entropy as a measure of electron correlation. The second-order entropy provides experimentally accessible information [35]. In Sec. IIIB the notation ΔS_{α} will be used to indicate the difference in the entropy in the presence and the absence of an electric field ϵ , $\Delta S_{\alpha} = S_{\alpha}(\epsilon) - S_{\alpha}(0)$. The α -order Rényi entropy of cluster formation is given by

$$S_{\alpha,\mathrm{f}} = S_{\alpha,\mathrm{cluster}} - \sum_{i} S_{\alpha,i},$$
 (5)

where the summation is over the entropy of each of the individual molecules. The summation is permissible due to the additivity of the Rényi entropy for noninteracting constituents. The entropy of formation quantifies the excess quantum correlation that exists in the cluster due to the intermolecular bonding. The von Neumann entropy is used to measure both electron correlation and entanglement for each molecule in Sec. IIIB while the second-order Rényi entropy is only employed to measure electron correlation and entanglement in the formaldehyde array.

B. Results

For both HeH⁺ and MgH⁺ the first-order Rényi entropy as a function of the field strength along and against the dipole moment is shown in Table I. As predicted by the theorem in Sec. II, the electron correlation, measured by the entropy, increases with the electric field in the direction against the dipole moment and decreases with the electric field in the direction of the dipole moment. While not shown, the Euclidean distance from the center of the 1-RDM set showed similar correlation trends as the entropy. The 1-RDM moves towards a noninteracting extreme point of the set as the expectation value of the one-body dipole moment increases. Figure 2 also shows that for HeH⁺ the expectation value of the Coulomb repulsion between a pair of electrons $1/r_{12}$ decreases with the field strength in the direction of the dipole moment $\theta = 0$ and increases with the electric field in the direction opposite to that of the dipole moment $\theta = \pi$, which is consistent with previous work showing a statistical relationship between r_{12} expectation values and electron correlation [36].

TABLE I. Dipole moments and entropies of HeH⁺ and MgH⁺ in the electric field (ϵ) are presented from p2-RDM calculations using the augmented cc-pVDZ basis set. The entropy decreases with the electric field in the direction of the dipole moment while the entropy increases with the electric field in the direction against the dipole moment. The changes in dipole moment and Rényi entropy are reported relative to zero-field values. Dipole moments are expressed in units of Debye (D), and the Rényi entropies are dimensionless.

	ϵ (a.u.)	$ \mu $	S_1	$\Delta \mu $	ΔS_1
HeH ⁺	0.015	1.9296	0.1316	0.1614	-0.0014
	0.010	1.8705	0.1321	0.1023	-0.0009
	0.000	1.7682	0.1330	0.0000	0.0000
	-0.010	1.6795	0.1333	-0.0887	0.0003
	-0.015	1.6389	0.1338	-0.1293	0.0008
MgH^+	0.015	4.7615	0.3449	1.1779	-0.0588
	0.010	4.4078	0.3602	0.8242	-0.0435
	0.000	3.5836	0.4037	0.0000	0.0000
	-0.010	2.5031	0.4763	-1.0805	0.0726
	-0.015	1.8224	0.5281	-1.7612	0.1244

Table II displays the change in the energies, dipole moments, and entropies of BH, HCN, H₂O, and HF with electricfield strength. The entropy decreases with the electric field in the direction of the dipole moment while the entropy increases with the electric field in the direction against the dipole moment. Figure 3 shows an approximately linear relationship between the change in the dipole moment and the change in the first-order Rényi entropy relative to the Rényi entropy at $\epsilon = 0$. While the computed results are approximately linear and monotonic, the theoretical results presented in the previous section do not require this relationship to be linear or even strictly monotonic.

Similar results are obtained for the molecule formaldehyde. We apply a homogeneous one-dimensional electric field of strength starting from $10^5 - 10^8$ V/m, as used in the experiment [37], and proceeding to 10^9 V/m. Table III shows that both



FIG. 2. For HeH⁺ the expectation value of the Coulomb repulsion between a pair of electrons $1/r_{12}$, reported in a.u. of energy, decreases with the field strength in the direction of the dipole moment $\theta = 0$ and increases with the electric field in the direction opposite to that of the dipole moment $\theta = \pi$.

TABLE II. Dipole moments and entropies of molecular systems in the electric field (ϵ) are presented from p2-RDM calculations using the augmented cc-pVDZ basis set. The entropy decreases with the electric field in the direction of the dipole moment while the entropy increases with the electric field in the direction against the dipole moment. The changes in dipole moment and Rényi entropy are reported relative to zero-field values. Dipole moments are expressed in units of Debye (D), and the Rényi entropies are dimensionless.

	ϵ (a.u.)	$ \mu $ (D)	S_1	$\Delta \mu $ (D)	ΔS_1
BH	-0.015	0.1036	1.0330	-1.2682	0.0626
	-0.005	1.0499	0.9903	-0.3219	0.0199
	0.000	1.3718	0.9704	0.0000	0.0000
	0.005	1.7156	0.9525	0.3438	-0.0179
	0.015	2.6268	0.9205	1.2550	-0.0499
HCN	-0.015	1.8065	1.4970	-1.2605	0.0132
	-0.005	2.1001	1.4882	-0.9669	0.0044
	0.000	3.0670	1.4838	0.0000	0.0000
	0.005	3.1707	1.4791	0.1037	-0.0046
	0.015	3.8377	1.4707	0.7707	-0.0131
H ₂ O	-0.015	1.3462	0.8144	-0.7215	0.0076
	-0.005	1.9534	0.8091	-0.1143	0.0023
	0.000	2.0677	0.8068	0.0000	0.0000
	0.005	2.1985	0.8048	0.1308	-0.0020
	0.015	2.2842	0.8017	0.2165	-0.0051
HF	-0.015	1.6620	0.6404	-0.2564	0.0050
	-0.005	1.8913	0.6368	-0.0271	0.0014
	0.000	1.9184	0.6354	0.0000	0.0000
	0.005	2.0155	0.6339	0.0971	-0.0015
	0.015	2.0454	0.6317	0.1270	-0.0037

the first-order and second-order Rényi entropies decrease with the electric field in the direction of the dipole moment while they increase with the electric field in the direction against the dipole moment. Importantly, the modulation of the electron



FIG. 3. The dipole moment relative to its value at $\epsilon = 0$ versus the first-order Rényi entropy relative to its value at $\epsilon = 0$ is shown for each of the molecules (a) BH, (b) HCN, (c) H₂O, and (d) HF. The data indicate an approximately linear relationship. For BH the Pearson correlation coefficient is 0.981 and the slope of the best-fit line is -23.69 a.u. The Rényi entropies are dimensionless.

TABLE III. Changes in the dipole moments and entropies of CH₂O and (CH₂O)₆ are reported as functions of the electric field ϵ relative to their values at zero field $\epsilon = 0$. In both cases the entropy decreases with the electric field in the direction of the dipole moment but increases with the electric field in the opposite direction. Dipole moments are expressed in units of Debye (D), and the Rényi entropies are dimensionless. The zero-field dipole moments of CH₂O and (CH₂O)₆ are 2.4263 and 13.9403 D, respectively. The 1-RDMs were computed from the a cc-pVDZ basis set using p2-RDM.

	ϵ (a.u.)	$\Delta \mu $ (D)	ΔS_1	ΔS_2
CH ₂ O	-0.015	-0.6337	0.0224	0.0007
	-0.005	-0.0808	0.0081	0.0002
	0.000	0.0000	0.0000	0.0000
	0.005	0.3407	-0.0064	-0.0003
	0.015	1.1097	-0.0208	-0.0007
$(CH_2O)_6$	-0.015	-3.8415	0.1517	0.0008
	-0.005	-2.6110	0.0484	0.0003
	0.000	0.0000	0.0000	0.0000
	0.005	1.5238	-0.0384	-0.0002
	0.015	4.2936	-0.1427	-0.0007

correlation by the electric field is applicable to not only individual molecules but also clusters of molecules.

Clusters of formaldehyde molecules were employed in cold-temperature experiments, first reported in 2003 [38] and perfected in 2016 using an electrostatic Sisyphus trap [37]. We consider the two-dimensional lattice of six formaldehyde molecules separated by 5.0 Å shown schematically in Fig. 4. As for the single formaldehyde molecule, Table III reveals that the Rényi entropies of the cluster decrease with the electric field in the direction of the dipole moment while they increase with the electric field in Fig. 5, the increase or decrease in the entanglement of the cluster system is amplified compared to that of the individual molecules at infinite separation. The electric field controls not only the electron correlation within the molecule but also the electronic entanglement of formaldehyde molecules.

We also examined the effect of the electric field on the electron correlation of larger molecules such as a fluorescent dye mimic of VF2.1.H [40,41], which has been used for sensing voltage in neurons [41]. Figure 6 displays the fluorescent dye mimic of VF2.1.H [40,41]. Table IV presents the first-order Rényi entropy as a function of the field in the directions parallel



FIG. 4. Schematic of the $(CH_2O)_6$ crystal from Jmol [39] is shown. The oxygen atoms are marked in red, the carbon atoms in gray, and the hydrogen atoms in black.



FIG. 5. The first-order Rényi entropies S_1 of the six noninteracting molecules and the cluster are shown as functions of the electric field in the direction of the dipole moment ($\theta = 0$) and in the direction opposite to the dipole moment ($\theta = \pi$). The cluster disentangles and entangles more in the field than the six noninteracting molecules, which indicates that the field cannot only decorrelate (correlate) the individual molecules but also disentangle (entangle) the molecules from each other. The Rényi entropies are dimensionless.

and antiparallel to the direction of the dipole moment. As seen in the other molecular systems, the electron correlation, measured by the entropy increases with the electric field in the direction opposite to that of the dipole moment and decreases with the electric field in the direction of the dipole moment. The change in entropy reflects the movement of the 1-RDM towards a noninteracting extreme point of its *N*-representable set as the expectation value of the one-body dipole moment increases.

IV. DISCUSSION AND CONCLUSION

The degree of electron correlation and entanglement in quantum molecular systems can be controlled through an



TABLE IV. Changes in the dipole moments and entropies of a fluorescent dye mimic of VF2.1.H are reported as functions of the electric field ϵ relative to their values at zero field $\epsilon = 0$. The entropy decreases with the electric field in the direction of the dipole moment but increases with the electric field in the direction against the dipole moment. Dipole moments are expressed in units of Debye (D), and the Rényi entropies are dimensionless.

ϵ (a.u.)	$ \mu $	$\Delta \mu $ (D)	S_1	ΔS_1
0.0100	42.4705	13.3129	12.3920	-0.1372
0.0075	40.2996	11.1419	12.4238	-0.1054
0.0050	38.6528	4.6908	12.4600	-0.0692
0.0010	29.3534	0.7957	12.5139	-0.0153
0.0000	29.1576	0.0000	12.5292	0.0000
-0.0010	26.6115	-2.5461	12.5451	0.0158
-0.0050	23.1638	-5.9938	12.6284	0.0992
-0.0075	18.3631	-10.7947	12.6960	0.1669
-0.0100	17.0677	-12.0899	12.7674	0.2382

external stimulus such as an electric field. We prove that any external stimulus that significantly changes the expectation value of a one-electron operator with nondegenerate minimum and maximum eigenvalues can be used to control the degree of electron correlation in the molecule. To obtain this result, we employ the convexity of the set of 1-RDMs and Coleman's theorem that the extreme 1-RDMs of the set are the uncorrelated 1-RDMs whose *N*-electron wave functions are Slater determinants. Using the electric field, for example, to steer the 1-RDM in the direction of the extreme 1-RDM where the dipole moment reaches its maximum value causes the quantum system to decorrelate.

The control of quantum molecular systems was demonstrated computationally with HeH⁺, MgH⁺, BH, HCN, H₂O, HF, CH₂O, a fluorescent dye, as well as an array of six CH₂O. Using the first-order and second-order Rényi entropies to quantify the degree of correlation, we observe that the degree of correlation can be decreased or increased through the application of a homogeneous electric field in the direction parallel or antiparallel to the molecule's intrinsic dipole moment. Using other metrics to quantify the electron correlation, such as the distance of the 1-RDM to the center of the convex set [42], leads to the same conclusions. The calculations with an array of formaldehyde molecules also show that the field can control not only the electron correlation of a formaldehyde molecule but also the entanglement among formaldehyde molecules in an array. Thereby, the external stimulus can also be employed to entangle or disentangle a set of molecules assembled by intermolecular forces or an optical trap. The control of a molecule's correlation and entanglement by an electric field has potential applications to designing molecules and materials with targeted properties, modifying the degree of correlation between fundamental units in quantum computation, and understanding the electric-field properties of biological systems, especially membranes.

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FIG. 6. A fluorescent dye mimic of VF2.1.H is shown.

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APPENDIX A: ELECTRON CORRELATION AS ENTANGLEMENT

Electron correlation is a form of quantum entanglement. For a pure state the definition of *entanglement* is that the density matrix cannot be written as a product of the density matrices of its subsystems. In the case of electron correlation the subsystem density matrices are the 1-RDMs in their natural-orbital (eigenfunction) basis set. Therefore, an N-electron quantum system is correlated if and only if its N-electron density matrix cannot be written as a product of the 1-RDMs in their natural-orbital basis set. This definition of electron correlation in the terminology of entanglement is equivalent to the conventional definition in which the wave function is inexpressible as a single Slater determinant. While entanglement is often associated with particles that are located at a great distance from each other, such large separation is not necessary for entanglement and not applicable in the case of electrons bound to a molecule [43]. Appendix B also shows that the *cumulant* of the 2-RDM is nonvanishing if and only if the N-electron density matrix is correlated. Furthermore, the von Neumann entropy of the 1-RDM is nonzero if and only if the cumulant of the 2-RDM does not vanish. Therefore, the von Neumann entropy of the 1-RDM is nonzero if and only if the quantum system exhibits electron correlation (entanglement of the N-electron density matrix with respect to the product of the 1-RDMs).

APPENDIX B: QUANTIFICATION OF ELECTRON CORRELATION

The cumulant (or connected) part $^{2}\Delta$ of the two-electron reduced density matrix (2-RDM) [5,44–46] is defined as

$${}^{2}\Delta_{kl}^{ij} = {}^{2}D_{kl}^{ij} - 2 {}^{1}D_{k}^{i} \wedge {}^{1}D_{l}^{j}$$
(B1)

in which ${}^{1}D$ and ${}^{2}D$ are the 1- and 2-RDMs, normalized to N and N(N - 1), and \wedge is the antisymmetric tensor product known as the Grassmann wedge product [5,47]. From the cumulant's definition in Eq. (B1) it can be shown that the trace

of the cumulant of the 2-RDM is nonpositive and equal to [48–50]

$$\operatorname{Tr}(^{2}\Delta) = -\operatorname{Tr}(^{1}D^{1}Q) \leqslant 0, \qquad (B2)$$

with ${}^{1}Q(={}^{1}I - {}^{1}D)$ being the 1-hole RDM in terms of the 1-RDM and the identity matrix ${}^{1}I$. Because ${}^{1}D$ and ${}^{1}Q$ are positive semidefinite, the trace of the cumulant 2-RDM vanishes if and only if ${}^{1}D$ and ${}^{1}Q$ lie in orthogonal subspaces which is equivalent to the *N* eigenvectors of the 1-RDM (natural orbitals) being completely filled and the remaining eigenvectors (natural orbitals) being completely empty or the 1-RDM being representable by an *N*-electron Slater determinant. Consequently, we have that the trace of the cumulant 2-RDM vanishes if and only if the *N*-electron quantum system is not correlated [48]. Furthermore, because the magnitude of the trace of the cumulant 2-RDM reflects the degree to which natural orbitals are shared by both particles and holes, it provides a mechanism to quantify the degree of electron correlation.

The trace of the cumulant can be related to the von Neumann entropy [1,2,29,30] in Eq. (3) The natural logarithm of the 1-RDM can be expanded in a power series about the identity matrix

$$\ln({}^{1}D) = \ln({}^{1}I - {}^{1}Q)$$
(B3)

$$= -\sum_{n=1}^{\infty} ({}^{1}\mathcal{Q})^{n}/n \tag{B4}$$

$$\approx -{}^{1}Q - O({}^{1}Q^{2}). \tag{B5}$$

Substituting Eq. (B5) into the von Neumann entropy in Eq. (3) and using Eq. (B2) yields

$$S_1 \approx -\operatorname{Tr}(^2 \Delta) + O\{\operatorname{Tr}[^1 D(^1 Q)^2]\} \ge 0.$$
 (B6)

Hence, we observe that the von Neumann entropy is equal to the negative of the trace of the cumulant 2-RDM through the terms scaling linearly with the 1-hole RDM. Like the negative of the trace of the cumulant 2-RDM, the von Neumann entropy is a nonnegative quantity which vanishes only in the absence of electron correlation. The von Neumann entropy of the 1-RDM has been employed extensively in the literature [33,34,50–58] as a measure of electron correlation.

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