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Manas Sajjan, Kade Head-Marsden, and David A. Mazziotti

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Entangling and Disentangling Many-electron Quantum Systems with an Electric Field

Manas Sajjan, Kade Head-Marsden and David Mazziotti*

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, IL 60637

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Electron correlation of a molecular system, we show, can be enhanced or diminished through the application of a homogeneous electric field anti-parallel 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 one-electron operator with non-degenerate 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, H_2O , HF, formaldehyde, and a fluorescent dye.. Furthermore, we show in calculations with an array of formaldehyde (CH_2O) 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 pure-state 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 many-electron 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.

The application of an electric field in the direction parallel to a molecule’s dipole moment, we show computationally, 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 non-degenerate 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, H_2O , HF, CH_2O , and a fluorescent dye. Furthermore, we show in calculations with formaldehyde (CH_2O) that the field can con-

trol not only the electron correlation of a formaldehyde 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.

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 non-degenerate 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 wavefunction

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

Such a 1-RDM is said to be *pure N -representable* [13–16]. 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 wavefunctions are Slater determi-

* damazz@uchicago.edu

nants [11, 13]. Formally, the convex set of ensemble N -representable 1-RDMs is the *convex hull* of its extreme 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:

$$\langle {}^1\hat{O} \rangle(\epsilon) = \text{Tr}({}^1\hat{O} {}^1D(\epsilon)) \quad (2)$$

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 ${}^1D(\epsilon)$ 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 non-degenerate 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, 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 non-degenerate 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 non-degenerate 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 non-degenerate 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 (maximum value) and its yellow color (minimum value) occurring at the 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.

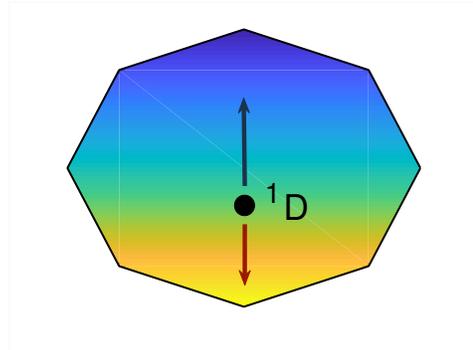


FIG. 1. A schematic representation of the convex set of 1-RDMs is depicted. The color scheme of the set is chosen to represent its convexity with the most blue color (minimum value) and its most yellow color (maximum value) occurring at the extreme points (extreme 1-RDMs) of the set. Changing the electric 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.

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 , H_2O , and HF , the formaldehyde molecule CH_2O and an array of 6 formaldehyde molecules CH_2O , 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 , H_2O , 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 two-electron reduced density matrix (2-RDM) method in which a parametrization of the 2-RDM is directly computed without the many-electron wavefunction [17–24]. The augmented correlation-consistent polarized valence double-zeta (aug-cc-pVDZ) 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 formaldehyde-cluster [25, 26], and the Dunning-Hay double-zeta basis set was employed for the dye mimic [27].

The degree of electron correlation in the 1-RDM is quantified through its the von Neumann entropy [28], equivalent to its first-order Rényi entropy [29],

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

or its second-order Rényi entropy [29–31].

$$S_2 = -\ln(\text{Tr}({}^1D^2)). \quad (4)$$

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 that 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 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, 32, 33]. 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 [34]. In section III B 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

$$S_{\alpha,f} = S_{\alpha,\text{cluster}} - \sum_i S_{\alpha,i}, \quad (5)$$

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 non-interacting 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 section III B 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 section 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 non-interacting 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 against the direction against the dipole moment $\theta = \pi$, which is consistent with previous work showing a statistical relationship between r_{12} expectation values and electron correlation [35].

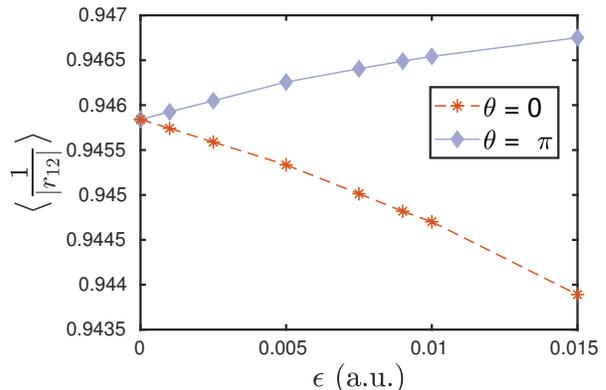


FIG. 2. For HeH^+ the expectation value of the Coulomb repulsion between a pair of electrons $1/r_{12}$, reported in a.u. of energy, decreases with the field strength in the direction of the dipole moment $\theta = 0$ and increases with the electric field against the direction against the dipole moment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

Table II displays the change in the energies, dipole moments, and entropies of BH, HCN, H_2O , and HF with electric-field 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

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 |

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.

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_2O | -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 |

Similar results are obtained for the molecule formalde-

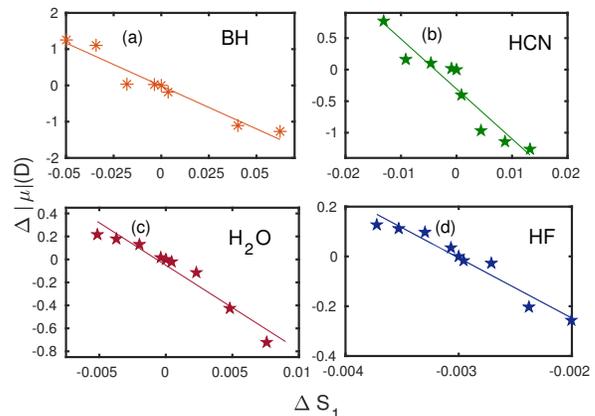


FIG. 3. The dipole moment relative to its value at $\epsilon = 0$ versus the first-order Rényi entropy relative to its value at $\epsilon = 0$ is shown for each of the molecules (a) BH, (b) HCN, (c) H_2O , and (d) HF. The data indicates an approximately linear relationship. For BH the Pearson correlation coefficient is 0.981 and the slope of the best-fit line is -23.69 a.u. The Rényi entropies are dimensionless.

hyde. We apply a homogeneous one-dimensional electric field of strength starting from 10^5 - 10^8 V/m, as used in experiment [36] and proceeding to 10^9 V/m. Table III shows that both 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 correlation by the electric field is applicable to not only individual molecules but also clusters of molecules.

Clusters of formaldehyde molecules have been employed in cold-temperature experiments, first reported in 2003 [37] and perfected in 2016 using an electrostatic Sisyphus trap [36]. 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 the opposite direction. Significantly, as displayed 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 [39, 40], which has been used for sensing voltage in neurons [40]. Figure 6 displays the fluorescent dye mimic of VF2.1.H [39, 40]. Table IV presents the first-order Rényi entropy as a function of the field strength along and against the dipole moment. As seen in the other molecular systems, the electron

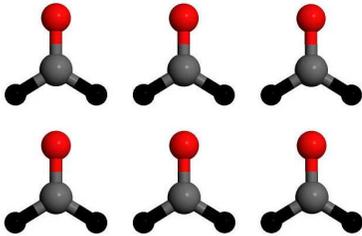


FIG. 4. Schematic of the $(\text{CH}_2\text{O})_6$ crystal from Jmol [38] is shown. The oxygen atoms are marked in red, the carbon atoms in grey and the hydrogens in black.

TABLE III. Changes in the dipole moments and entropies of CH_2O and $(\text{CH}_2\text{O})_6$ 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 direction against the dipole moment. Dipole moments are expressed in units of Debye (D), and the Rényi entropies are dimensionless. The zero-field dipole moments of CH_2O and $(\text{CH}_2\text{O})_6$ are 2.4263 D 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_2O | -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 |
| $(\text{CH}_2\text{O})_6$ | -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, 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. The change in entropy reflects the movement of the 1-RDM towards a non-interacting extreme point of its N -representable set as the expectation value of the one-body dipole moment increases.

IV. DISCUSSION AND CONCLUSIONS

The degree of electron correlation and entanglement in quantum molecular systems can be controlled through an external stimulus such as an electric field. We proved that any external stimulus that significantly changes the expectation value of a one-electron operator with non-degenerate minimum and maximum eigenvalues can be

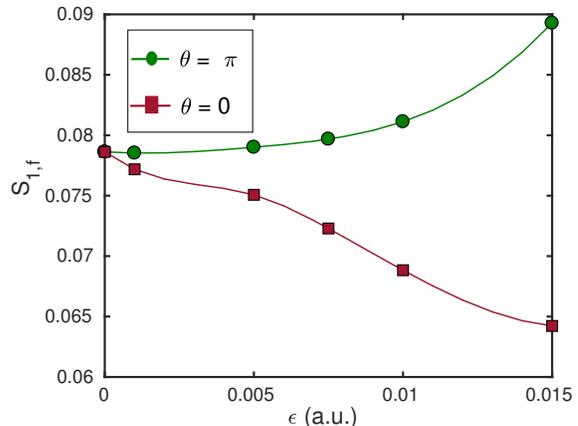


FIG. 5. The first-order Rényi entropies S_1 of the six noninteracting molecules and the cluster are shown as functions of the electric field in the direction of the dipole moment ($\theta = 0$) and in the direction opposite to the dipole moment ($\theta = \pi$). The cluster disentangles and entangles 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.

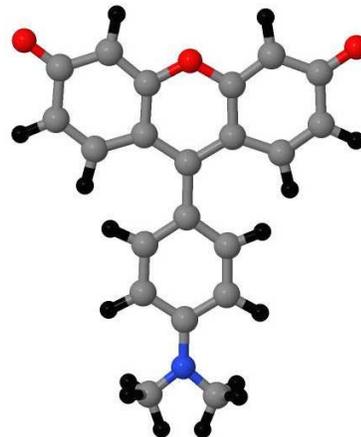


FIG. 6. A fluorescent dye mimic of VF2.1.H is shown.

used to control the degree of electron correlation in the molecule. To obtain this result, we employed 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 wavefunctions 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 , H_2O , HF , CH_2O , a fluorescent dye, as well as an array of six CH_2O . Using the first-order and second-order

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 |

Rényi entropies to quantify the degree of correlation, we observed that degree of correlation could be decreased or increased through the application of a homogeneous electric field in the direction parallel or anti-parallel 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 [41], led to the same conclusions. The calculations with an array of formaldehyde molecules also showed that 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 in a cluster or synthetically by 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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Appendix A: Electron Correlation as Entanglement

Electron correlation is a form of quantum entanglement. For 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 wavefunction 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 [42]. Appendix B also shows that the *cumulant* of the 2-RDM is non-vanishing 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, 43–45] is defined as

$${}^2\Delta_{kl}^{ij} = {}^2D_{kl}^{ij} - 2 {}^1D_k^i \wedge {}^1D_l^j \quad (\text{B1})$$

in which 1D and 2D 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, 46]. 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 [47–49]

$$\text{Tr}({}^2\Delta) = -\text{Tr}({}^1D {}^1Q) \leq 0 \quad (\text{B2})$$

with ${}^1Q (= {}^1I - {}^1D)$ being the 1-hole RDM in terms of the 1-RDM and the identity matrix 1I . Because 1D and 1Q are positive semidefinite, the trace of the cumulant 2-RDM vanishes if and only if 1D and 1Q 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 [47]. 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, 28, 29] in Eq. (3) The natural

logarithm of the 1-RDM can be expanded in a power series about the identity matrix

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

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

$$\approx -{}^1Q - \mathcal{O}({}^1Q^2). \quad (\text{B5})$$

Substituting Eq. (B5) into the von Neumann entropy in

Eq. (3) and using Eq. (B2) yields

$$S_1 \approx -\text{Tr}({}^2\Delta) + \mathcal{O}(\text{Tr}({}^1D({}^1Q)^2)) \geq 0. \quad (\text{B6})$$

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 [32, 33, 49–57] as a measure of electron correlation.

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