Classical and Quantum Orbital Correlations in the Molecular Electronic States

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The quantum superposition principle has been extensively utilized in the quantum mechanical description of the bonding phenomenon. It explains the emergence of delocalized molecular orbitals and provides a recipe for the construction of near-exact electronic wavefunctions. On the other hand, its existence in composite systems may give rise to nonclassical correlations that are regarded now as a resource in quantum technologies. Here, we approach the electronic ground states of three prototypical molecules from the point of view of fermionic information theory. For the first time in the literature, we properly decompose the pairwise orbital correlations into their classical and quantum parts in the presence of superselection rules. We observe that quantum orbital correlations can be stronger than classical orbital correlations though not often. Also, quantum orbital correlations can survive even in the absence of orbital entanglement depending on the symmetries of the constituent orbitals. Finally, we demonstrate that orbital entanglement would be underestimated if the orbital density matrices were treated as qubit states.

I. INTRODUCTION

One of the principal contributions of quantum mechanics to chemistry has been the description of chemical bonding as the quantum superposition phenomenon [1]. In valence bond (VB) theory [2], the increase in the stability of bonded atoms originates from the superposition of alternative electronic structures known as VB or resonance structures. Molecular orbital theory [3] suggests a different description for the same reality. What stabilizes the interacting atoms by a certain amount of energy is the delocalization of the electrons participating in this interaction throughout the molecule. Namely, the electrons occupy delocalized orbitals made from the quantum superposition of atomic orbitals. These two quantum mechanical theories are equivalent to each other at the limit [4, 5], and both explain the stability of molecules as a decrease in energy due to the principle of quantum superposition.

The quantum states that arise from the quantum superposition principle are now regarded as a resource as real as energy for new quantum technologies [6]. Quantum coherence and correlations [7, 8] are the characteristic traits of such states that enforce the entire departure of quantum materials from classical lines of thought.

The quantum entanglement is considered to be the perfect example of quantum correlations and its role as a resource in quantum technologies is well established [9–11]. However, it constitutes only a subset of the most general quantum correlations known as quantum discord [12, 13]. The discord can survive in the dissipative environments that wash away all the entanglement [14]. Also, it can serve a useful role as a resource in some tasks that are otherwise impossible, even in the absence of the entanglement. These include the detection of quantum phase transitions [15], the remote state preparation for quantum information processing [16], the secure quantum key distribution in quantum cryptography [17, 18], the noisy protocols in quantum communication [19], the interferometric schemes in quantum metrology [20–22], and the micro- and nanoscale heat flow control in quantum thermodynamics [23, 24].

Besides its resourcefulness in quantum technologies, the notion of correlation is central to many contemporary fields and has been extended to quantum chemistry since the early 2000s. In particular, the quantum chemistry version of density matrix renormalization group algorithm [25, 26] has been optimized based on the numerical methods [27–31] that quantify the pairwise orbital correlations in terms of the quantum mutual information. Moreover, this information-theoretical quantity also has been proposed to investigate the nature of the chemical bonding in different molecular structures [32–38]. However, although the quantum mutual information is a measure of the total correlations between two subsystems [12, 13], the orbital correlations quantified by it have been referred to orbital entanglement until recently.

Ref. [39] attempted to separate orbital-orbital correlations into classical and quantum parts for the first time in the literature. However, the classical orbital correlations were explored by a distance-based measure, which was first proposed by one of us in Ref. [12] and quantifies both classical and quantum correlations excluding the entanglement [40]. Here, we present a proper decomposition of the total orbital correlations into its classical and quantum parts using the original definition of quantum discord [12, 13] that depends on the difference between two different quantum generalizations of mutual information. Also, we demonstrate whether orbital discord includes orbital entanglement or not by checking the fermionic version of the logarithmic entanglement negativity [41–44].

The paper is organized as follows. After giving a brief introduction to the fermionic information theory, describing the orbitals as two-mode subsystems in Sec. II A and discussing the superselection rules imposed on them in Sec. II B, we will present the quantification of orbital discord explicitly in Sec. II C. Section II D outlines the quantification of orbital

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entanglement based on the fermionic partial transpose. The quantum discord and entanglement shared between the orbitals of some prototypical molecules are identified in Sec. III. We discuss our main results and take a look to future research directions in Sec. IV. We conclude with a summary in Sec. V.

II. METHODS

In this part of the paper, we will detail the concepts and methods that are essential for our investigation of the correlations shared between the Hartree-Fock (HF) molecular orbitals (MOs) of the water molecule H$_2$O, 2-propenyl C$_3$H$_5$, and dicarbon anion C$_2^-$. The geometries of all these prototypical molecules were optimized at HF/STO-6G level of theory, and they were assumed to be prepared in their electronic ground states. Specifically, we examined the *ab initio* ground states calculated by using the configuration interaction (CI) method [45–47] and considered only the single and double excitations (CISD) above the HF reference state as below:

\[
|\Psi\rangle = \frac{1}{N} \left( I + \sum_{i,a} c_i^a f_i^a f_i^\dagger + \sum_{i>j,a>b} c_{i,j}^{a,b} f_i^a f_j^b f_i^\dagger f_j^\dagger \right) |\Psi_{\text{HF}}\rangle. \tag{1}
\]

In this above equation, $N$ is the normalization constant, $\{c\}$ are the coefficients optimized according to the Rayleigh-Ritz variational principle in the Gaussian09 programme suite [48], where the subscripts and superscripts of these coefficients stand respectively for the occupied and vacant spin-orbitals (fermionic modes) in the reference state, and $f_i^\dagger$ ($f_i$) is the operator that creates (annihilates) an electron in the $\mu$th mode and obeys the fermionic anticommutation relations

\[
\{f_\mu, f_\nu\} = \{f_\mu^\dagger, f_\nu^\dagger\} = 0, \quad \{f_\mu, f_\nu^\dagger\} = \delta_{\mu\nu}. \tag{2}
\]

A. Reduced States of Orbitals

Each separate term in the expanded form of Eq. (1) is known as an “configuration” and corresponds to a Slater determinant, which is an antisymmetrized product of HF spin-orbitals $\{\psi_\mu\}$. Assuming there are $n_e$ electrons and $n$ MOs in the molecule, the dominant configuration $|\Psi_{\text{HF}}\rangle$ can be written in the $2n$-mode fermionic Fock space as

\[
|\Psi_{\text{HF}}\rangle = f_{\mu_1}^\dagger \cdots f_{\mu_n}^\dagger f_{\nu_1} f_{\nu_2} \cdots f_{\nu_{2n}} |\Omega\rangle,
\]

where $\psi_{2\mu-1}$ and $\psi_{2\mu}$ are the $\mu$th spin-up and spin-down HF orbitals, the double-lined Dirac notation $|\cdot\rangle$ denotes the states in the fermionic Fock space, $|\Omega\rangle$ represents the vacuum state, and the wedge product $\wedge$ provides the antisymmetrization imposed by the anti-commutation relations, e.g.,

\[
|\psi_\mu\rangle \wedge |\psi_\nu\rangle = \frac{1}{\sqrt{2}} \left( |\psi_\mu\rangle \otimes |\psi_\nu\rangle - |\psi_\nu\rangle \otimes |\psi_\mu\rangle \right).
\]

Using the occupation number representation introduced in Eq. (3), we rewrote the post-HF ground state (1) as

\[
|\Psi\rangle = \sum_{\vec{s}} \lambda_{\vec{s}} (f_{2n}^\dagger)^{s_{2n}} \cdots (f_2^\dagger)^{s_2} (f_1^\dagger)^{s_1} |\Omega\rangle
= \sum_{\vec{s}} \lambda_{\vec{s}} \sum_{s_1} \cdots \sum_{s_{2n}} |P_{s_1,\ldots,s_{2n}}\rangle |\psi_{s_1}\psi_{s_2}\cdots\psi_{s_{2n}}\rangle,
\]

with $\vec{s} = \{s_1, s_2, \ldots, s_{2n}\}$, $\sum_{\mu=1} s_\mu = n_e$, and $s_\mu \in \{0, 1\}$. Here, $\lambda_{\vec{s}} = (-1)^{k_{\vec{s}}(\vec{s})}/N$ where $k_{\vec{s}}$ equals to $n_{\mu - \nu} - i$ and $i + j$ for the single and double excitation configurations, respectively. Then, we constructed the following $2^{2n} \times 2^{2n}$ density matrix

\[
\rho = |\Psi\rangle\langle |\Psi| = \sum_{\vec{s},\vec{r}} \lambda_{\vec{s}} \lambda_{\vec{r}} (f_{2n}^\dagger)^{s_1} \cdots (f_{2n}^\dagger)^{s_{2n}} |\Omega\rangle\langle |\Omega| (f_{2n})^{r_1} \cdots (f_{2n})^{r_{2n}}
= \sum_{\vec{s},\vec{r}} \lambda_{\vec{s}} \lambda_{\vec{r}} |s_1 \cdots s_{2n}\rangle \langle r_1 \cdots r_{2n}| |\psi_{s_1} \cdots \psi_{s_{2n}}\rangle \langle r_1 \cdots r_{2n}| |\psi_{r_1} \cdots \psi_{r_{2n}}\rangle
\]

and stored only its non-zero elements for further calculations using the triplet sparse matrix representation below

\[
\rho = \{\lambda_{\vec{s}} \lambda_{\vec{r}}, \vec{s}, \vec{r}\}. \tag{7}
\]

Next, single and two-orbital reduced states were calculated by taking the partial trace of the state $\rho$ given in Eq. (6) over the modes $M = \{\mu_1, \ldots, \mu_M\}$ of the remaining orbitals. To this end, we exploited the inside out fermionic partial trace operation [49, 50] which is given by

\[
\sigma = \text{tr}_M[\rho] = \text{tr}_{\mu_1} \circ \text{tr}_{\mu_2} \circ \cdots \circ \text{tr}_{\mu_M}[\rho],
\]

where the single-mode partial trace operation reads

\[
\text{tr}_\mu[|s_1 \cdots s_{2n}\rangle \langle r_1 \cdots r_{2n}| |\psi_{s_1} \cdots \psi_{s_{2n}}\rangle \langle r_1 \cdots r_{2n}| |\psi_{r_1} \cdots \psi_{r_{2n}}\rangle]
= \delta_{\mu, r_\mu} (-1)^k |s_1 \cdots s_{2n}\rangle \langle r_1 \cdots r_{2n}| |\psi_{s_1} \cdots \psi_{s_{2n}}\rangle \langle r_1 \cdots r_{2n}| |\psi_{r_1} \cdots \psi_{r_{2n}}\rangle, \tag{9}
\]

with $k^s = s_\mu \sum_{\nu < \mu} s_\nu + r_\mu r_\mu \sum_{\nu < \mu} r_\nu$.

B. Superselection Rules

Both the qubits and fermionic modes are two-level distinguishable quantum systems. However, the Jordan-Wigner transformation that maps fermions into qubit systems leads to some ambiguities arising from the absence of a consistent subsystem definition [49, 51–53]. This is why we need to modify the partial trace operation for fermions by a phase factor in Eq. (9). Besides, the superselection rules (SSRs) place additional constraints on the fermionic state space [54]. Although any superposition in the form of $\sum_{\vec{s}} \lambda_{\vec{s}} |s_1 \cdots s_{2n}\rangle$ is a valid quantum state for qubit systems, the nature does not allow a fermionic system to exist in all possible superpositions $\sum_{\vec{s}} \lambda_{\vec{s}} |s_1 \cdots s_{2n}\rangle$. This is related to the conservation of some physical quantities $Q$ by the systems under consideration. Mathematically, Q-SSR forces any valid quantum state $\rho$ to be block-diagonal with respect to the operator $Q$, i.e., $[\rho, Q] = 0$.

Parity (P) and particle number (N) are the most relevant observables for the ground state of common molecular systems,
the right orbital. The state $\rho = \{ \Pi_{L}, \Pi_{R} \}$ satisfies the joint Fock space constraint (6) and can be viewed as a projection onto the left orbital, given the complete set of measurements $\{ \Pi_{L} \}$ on the right orbital. The state $\rho_{L} = \rho_{L|R} \Pi_{R} / p_{LR}$ is the post-measurement state of the left orbital with corresponding probability $p_{LR} = \text{tr}_{LR}[\Pi_{L} \rho_{LR}]$. Physically, Eq. (13) identifies the amount of the maximum information about the left orbital that can be extracted after the measurements $\{ \Pi_{LR} \}$ performed on the right orbital and called as “right-classical” correlation. Similarly, when the shared correlations between the orbitals are extracted by performing local measurements on the left orbital one can end up with “left-classical” correlation. It is obvious that $C(R) \neq C(L)$ in general.

We then quantified the quantum correlations between the orbitals $L$ and $R$, where it is given by the difference between two different quantum generalizations of mutual information given by Eqs. (12) and (13):

$$D(R) = I - C(R) = S(\rho_{R}) - S(\rho_{LR}) + \min_{\{\Pi_{LR}\}} \left( \sum_{i_{R}} p_{i_{R}} S(\rho_{L|i_{R}}) \right).$$

By definition, quantum discord is asymmetric under the change $L \leftrightarrow R$. In simple terms, right and left quantum discord — $D(R)$ and $D(L)$, respectively — do not necessarily reveal the same amount of quantum correlation since the definition of the conditional entropy involves a measurement on one orbital (in Eq. (14) right orbital). We calculated both right and left quantum discord.

Let us elaborate on the optimization used in the proper decomposition of the total correlations into classical and quantum parts. The number of parameters required in this optimization is greatly reduced in the presence of SSRs. P-SSR only allows the measurements $\{ \Pi_{LR} \}$ performed in the basis

$$\{ |\alpha_{1} \rangle \}_{\alpha_{1}} \supseteq \{ |00 \rangle, |11 \rangle \},$$

which means that the optimization involves eight real parameters. On the other hand, N-SSR is conserved only if the measurements $\{ \Pi_{LR} \}$ are carried out in the basis

$$\{ |\beta_{1} \rangle \}_{\beta_{1}} \supseteq \{ |00 \rangle, |11 \rangle \},$$

which in turn decreases the number of optimized real parameters down to four.

D. Quantum Entanglement

Quantum discord includes the quantum entanglement as a subset. Whenever the state is inseparable, the ratio of $D$ to $I$ is the only true measure of how much of the total correlation is quantum entanglement. However, quantum correlations are not limited to quantum entanglement and separable mixed states can also possess nonclassical correlations. Discord covers such quantum correlations as well. That is to say, some orbital pairs can still display quantum correlations even they are not entangled.
TABLE I. Classical and quantum correlations between Hartree-Fock orbital pairs in the ground state of H$_2$O. Here, $I$ represents the exact value of the total correlation without SSR and $I_{P/N}$ equals to its fraction remaining in the presence of P/N-SSR. Both are quantified by the mutual information but only the latter is further decomposed into classical correlation (C) [12] and quantum discord (D) [12, 13]. The measurements performed on the left (L) and right (R) orbitals give the same amount of correlations in the presence of N-SSR. Quantum entanglement $E$ and its fractions $E_{P/N}$ in the presence of P/N-SSR are quantified by the fermionic entanglement negativity [41–44].

| $(L|R)$ | $I$ | $I_{P/N}$ | $I_{P/N}$ | $I_{P/N}$ | $E$ |
|-------|-----|----------|----------|----------|----|
| (2, 3) | $0.21 \times 10^1$ | 100% | 73.8% | 73.8% | 26.2% | 26.2% | 84.1% | 73.7% | 10.4% | 0.35 $\times 10^{-2}$ | 100% | 99.3% |
| (2, 4) | $0.32 \times 10^1$ | 100% | 73.8% | 35.7% | 73.8% | 21.2% | 21.2% | 42.6% | 35.6% | 7.0% | 0.92 $\times 10^{-2}$ | 34.8% | 34.6% |
| (2, 5) | $0.19 \times 10^2$ | 100% | 0.8% | 0.5% | 99.2% | 99.5% | 99.2% | 99.5% | 0.37% | 0.37% | 0.0% | 0.28 $\times 10^{-5}$ | 100% | 0.0% |
| (2, 6) | $0.48 \times 10^1$ | 99.4% | 76.3% | 74.3% | 23.1% | 25.1% | 74.8% | 74.3% | 1.0% | 0.81 $\times 10^{-1}$ | 98.2% | 98.2% |
| (2, 7) | $0.19 \times 10^1$ | 100% | 82.9% | 87.5% | 17.1% | 12.5% | 80.3% | 77.8% | 25.0% | 0.33 $\times 10^{-1}$ | 100% | 0.0% |
| (3, 4) | $0.94 \times 10^1$ | 100% | 79.4% | 79.3% | 20.6% | 20.7% | 88.1% | 79.1% | 9.0% | 0.13 $\times 10^{-1}$ | 100% | 98.9% |
| (3, 5) | $0.20 \times 10^2$ | 100% | 3.1% | 1.5% | 96.9% | 98.5% | 96.9% | 98.5% | 0.0% | 0.13 $\times 10^{-4}$ | 100% | 0.0% |
| (3, 6) | 0.13 | 100% | 87.8% | 87.6% | 12.2% | 12.4% | 83.9% | 82.4% | 15.0% | 0.10 | 100% | 0.0% |
| (3, 7) | 0.23 | 99.9% | 72.8% | 73.3% | 27.1% | 26.6% | 70.7% | 69.8% | 0.9% | 0.24 | 93.9% | 0.4% |
| (4, 5) | $0.29 \times 10^2$ | 100% | 1.9% | 1.0% | 98.1% | 99.0% | 98.1% | 99.0% | 0.7% | 0.0% | 0.12 $\times 10^{-4}$ | 100% | 0.0% |
| (4, 6) | 0.14 | 98.1% | 78.0% | 74.3% | 20.1% | 23.8% | 75.5% | 74.3% | 1.2% | 0.21 | 69.3% | 0.5% |
| (4, 7) | 0.10 | 100% | 81.2% | 83.5% | 18.8% | 16.5% | 77.3% | 75.8% | 15.0% | 0.11 | 100% | 0.0% |
| (5, 6) | $0.11 \times 10^1$ | 100% | 37.7% | 62.0% | 62.3% | 38.0% | 33.9% | 33.9% | 0.0% | 0.58 $\times 10^{-1}$ | 100% | 0.0% |
| (5, 7) | $0.20 \times 10^2$ | 100% | 38.3% | 61.2% | 61.7% | 38.8% | 16.0% | 16.0% | 0.0% | 0.17 $\times 10^{-1}$ | 100% | 0.0% |
| (6, 7) | 0.13 | 100% | 85.1% | 85.1% | 14.9% | 14.9% | 93.1% | 85.0% | 8.1% | 0.17 $\times 10^{-1}$ | 100% | 99.0% |

To check the separability of a discordant orbital pairs, we exploited the fermionic partial transpose proposed and investigated in Refs. [41–44]. Likewise the fermionic partial trace in Eq. (9), the most foundational distinction that separates the fermionic partial transpose from the qubit partial transpose is a phase factor as below:

$$\left\langle \frac{\sum_{s\in S_L}\sum_{r\in S_R} s_{L_1}s_{L_2}\cdots s_{L_M}r_{R_1}r_{R_2}\cdots r_{R_N}}{\sum_{s\in S_L}\sum_{r\in S_R} s_{L_1}s_{L_2}\cdots s_{L_M}r_{R_1}r_{R_2}\cdots r_{R_N}} \right\rangle = 1$$

(17)

$$(-1)^\phi \hat{U}_R \frac{\sum_{s\in S_L}\sum_{r\in S_R} s_{L_1}s_{L_2}\cdots s_{L_M}r_{R_1}r_{R_2}\cdots r_{R_N}}{\sum_{s\in S_L}\sum_{r\in S_R} s_{L_1}s_{L_2}\cdots s_{L_M}r_{R_1}r_{R_2}\cdots r_{R_N}} \hat{U}_R^\dagger,$$

where

$$\phi = \frac{(\tau_R + \bar{\tau}_R) \text{mod} 2}{2} + \frac{(\tau_R + \bar{\tau}_R)}{2} (\tau_L + \bar{\tau}_L),$$

(18)

with $\tau_{L(R)} = \sum_{L(R)} s_{LL(R)}, \bar{\tau}_{L(R)} = \sum_{L(R)} r_{RR(L)}$, and $\hat{U}_R = \prod_{j=1}^{N-SSR} (f_j + f_j^\dagger)$. As we focused on the pairwise orbital correlations, we considered only the bipartitions $L|R$ defined by $L_M = R_2$ in this paper. Then we calculated the fermionic logarithmic negativity proposed and investigated in Refs. [41–44], that reads

$$E = \log_2 \| \rho^{LR}_{\text{TP}} \|,$$

(19)

where $\| \rho \|$ denotes the trace norm that equals to $\text{tr}[(\sqrt{\rho^\dagger \rho})^{1/2}]$.

It is important to note that we utilized this measure not to quantify orbital-orbital entanglement but to reveal the nature of the orbital correlations quantified by quantum discord. The amount of quantum discord calculated by Eq. (14) was recognized as quantum entanglement for non-zero values of $E$. On the other hand, the value determined by $D$ was regarded as quantum correlations beyond entanglement when $E$ vanishes.

At this point, we should also emphasize that SSRs are believed to force the fermionic systems not to exist in bound entangled states that cannot be captured by the measure $E$ [44].

III. RESULTS

In what follows we present the total, classical, and quantum correlations between the pairs of the MOs of the ground states of the water molecule H$_2$O, 2-propenyl C$_3$H$_3$, and dicarbon anion C$_2^-$. Although the CIOSD ground states include all the HF MOs approximated in the STO-6G minimal basis set, we exclude the frozen orbitals while visualizing our data in the next three sections.

A. Water

As shown in Fig. 1, the electronic structure of water molecule H$_2$O consists of 10-electrons and 7 HF MOs. Here, the 1s$_1$, 2s$_1$, 1b$_2$, 2a$_1$, 1b$_1$, 4s$_1$, and 2b$_2$ orbitals are indexed in ascending order from 1 to 7. The geometry is defined by the bond length and the bond angle that are 1.02Å and 96.8°, respectively, and the CISO energy is converged to $-75.737545702 E_h$.

Details of the numerical results are given in Table I. There, the exact values of the total correlation $I$ and entanglement $E$ without SSR accompany their fractions remaining in the presence of SSRs. Further, Table I contains what percentage of the total correlation decomposes into classical correlation and quantum discord in the presence of the local P-SSR and N-SSR.
FIG. 1. The pairwise total correlations in the singlet ground state of H$_2$O and their proper decomposition into classical correlations and quantum discord in the presence of superselection rules (SSRs). The quantum discord is simply quantum entanglement for the pairs that share nonzero logarithmic negativity on the left panel. Otherwise, it quantifies quantum correlations beyond entanglement.

We have two particularly noteworthy results that should be mentioned here. First, even though the classical part tends to predominate the total correlation, there exist some cases with quantum discord as the dominant correlation in the presence of the local P-SSR. The cases in question are the pairs including the 5th orbital $1b_1$.

The $1b_1$ is the HOMO of the HF ground state and completely formed from the $2p_y$ electron lone pair of the oxygen atom. However, when the second orbital in the pair is one of the highest MOs indexed by 6 and 7, the dominance of quantum correlations holds only for the left-discord. That is to say, the quantum correlations can be stronger than the classical correlations for the pairs (5, 6) and (5, 7) only if the extraction of the latter is performed by the local measurements on the lone-pair orbital $1b_1$. Note that 6th and 7th orbitals participating in these pairs are $4a_1$ and $2b_2$, and have an antibonding character.

Second, after applying the local N-SSR, quantum discord between the pairs (2, 7), (3, 6), and (4, 7) survives even in the absence of entanglement. The 2nd and 3rd orbitals are bonding MOs $2a_1$ and $1b_2$, while the 4th orbital $3a_1$ has a character closer to a lone-pair MO than a bonding MO. Hence, these discordant pairs are composed of occupied and vacant HF MOs that have opposite $a_1/b_2$ symmetries.

B. 2-Propenyl

The bond lengths and angles between the neighboring carbon atoms in C$_3$H$_5$ are respectively 1.41 Å and 124.4° in the geometry optimized with the STO-6G minimal basis set. The electronic structure of the molecule involves 23-electrons and 20 HF MOs, with the final energy of $-116.35450180 \, E_h$.

In Fig. 2, the total correlation without SSRs reaches its
FIG. 2. The pairwise total correlations in the doublet ground state of C$_3$H$_5$ and their proper decomposition into classical correlations and quantum discord in the presence of superselection rules (SSRs). The quantum discord is simply quantum entanglement for the pairs that share nonzero logarithmic negativity on the left panel. Otherwise, it quantifies quantum correlations beyond entanglement.

maximum value 0.49 and minimum value 0.00097 for the pairs of orbitals (11, 13) and (11, 17), respectively. Obviously, the classical part of the total correlation is more dominant for all pairs of orbitals.

The quantum entanglement and discord possessed by the pairs of orbitals (11, 12) and (12, 13) are robust against local SSRs. As a matter fact, the orbital 12 does not share a non-negligible amount of logarithmic entanglement negativity with those other than 11 and 13. Also, the pair (11, 13) has quantum discord in the presence of the local N-SSR, though it exist in a separable state. These three orbitals share a unique symmetry different from the rest. Each of them is a superposition of only the three 2$p_z$ orbitals of carbon atoms, and therefore, they display a $\pi$-orbital character. Moreover, they respectively correspond to HOMO, half-filled MO, and LUMO in the HF ground state.

Besides, although they do not have any entanglement with or without SSRs, the pairs of orbitals (7, 13), (8, 13), (9, 13), (10, 13), (11, 14), and (11, 17) always have a nonzero quantum discord. Finally, under the local N-SSR, the ground state of C$_3$H$_5$ reveals 51 other orbital pairs exhibiting quantum discord in the absence of entanglement (more details can be seen in Fig. 2).

C. Dicarbon anion

The interatomic distance is 1.25Å in the optimized molecular geometry of the dicarbon anion C$_2^-$ in its doublet ground state. The electronic structure is composed of 13-electrons and 10 orbitals, with the final energy of $-75.293354472 \text{E}_\text{h}$. The numerical values of the total correlation without SSRs lie in the range between 0.00025 and 0.2 corresponding to the pairs of orbitals (3, 4) and (7, 8), respectively. The former is the only pair whose dominant pairwise correlation is quantum discord in the presence of the local P-SSR. Also, its discord does not vanish under the local N-SSR while its entanglement negativity is always small enough to be neglected. Actually, the 3rd and 4th orbitals that constitute this pair are the HF MOs $2\sigma_g$ and $2\sigma_u^*$. The simultaneous occupancy of these two orbitals, which has a probability of 0.91 in the ground state, implies the absence of a $\sigma$ bond between the C atoms and
FIG. 3. The pairwise total correlations in the doublet ground state of $\text{C}_2^-$ and their proper decomposition into classical correlations and quantum discord in the presence of superselection rules (SSRs). The quantum discord is simply quantum entanglement for the pairs that share nonzero logarithmic negativity on the left panel. Otherwise, it quantifies quantum correlations beyond entanglement.

reduces the bond order of the molecule.

As shown in Fig. 3, the orbitals 5, 6, and 7 do not share any quantum correlation with the other ones under the local SSRs. These orbitals are HOMO, half-filled MO, and LUMO in the HF ground state. Besides, each of them is composed of $\alpha$ and $\beta$ modes having incompatible symmetries (please see the red, purple, and green arrow pairs in Fig. 4). The 5th and 7th orbitals are mixtures of $\sigma_g$ and $\pi_u$ symmetries. The former (latter) includes a $3\sigma_g$ ($\beta$) mode and a $1\pi_u$ ($\alpha$) mode. Both modes in the 6th orbital possess $\pi_u$ symmetry, but the $\alpha$ and $\beta$ modes are symmetric superpositions of the two $2p_y$ and the two $2p_x$ orbitals of carbon atoms, respectively. Please note that these six $\alpha$ and $\beta$ modes are ordered differently in the neutral dicarbon molecule and constitute two degenerate $1\pi_u$ orbitals and one $3\sigma_g$ orbital, which are HOMOs and LUMO of the molecule, respectively.

Quantum discord in the pairs of orbitals (3, 8) and (3, 9) exist despite the lack of entanglement in the presence of the local N-SSR. The 3rd orbital is the bonding $\sigma$ orbital ($2\sigma_g$), while the 8th and 9th ones are degenerate antibonding $\pi$-orbitals ($1\pi_u^*$). Furthermore, the pairwise quantum correlations distributed among the antibonding orbitals 8, 9, and 10 seem not to be affected significantly by the local SSRs. These three orbitals are the unoccupied MOs in the HF ground state. The last one is $3\sigma_g^*$.

IV. DISCUSSIONS

A natural question to ask at this point is that what would happen if the density matrix of an orbital pair described a qubit system? To address this question, we recalculated the entanglement in two-orbital density matrices using the multipartite entanglement measure proposed in Ref. [55]. This measure becomes the negativity for two-qubit states and is easily computable using the code provided in Ref. [56], together with the parser YALMIP [57] and the solver SDPT3 [58, 59]. Then it turns out that some density matrices with fermionic mode entanglement are separable for qubit systems (see Supplementary Material for more details). It means that the orbital entanglement would be underestimated if the orbital density matrices were treated as qubit states.
FIG. 4. The orbital correlations in the doublet ground state of C$_2^-$ in the case when the mode pairs with the same symmetry are considered as subsystem as in the singlet state of C$_2$. The orbitals 5, 6, and 7 in Fig. 3 consist of the α and β modes represented by red, purple, and green up and down arrow pairs, respectively. However, the HF MOs in the ground state of C$_2$ are composed of the mode pairs sharing the same symmetry, i.e., they are two degenerate 1π$_u$ orbitals and one 3σ$_g$ orbital highlighted in blue, orange, and black in the energy diagram.

Another fundamental question that we can ask here is how the chosen orbital basis affects the classical and quantum orbital correlations. Here, we have so far investigated the correlations between HF MOs, which are also known as delocalized or canonical MOs. These orthogonal orbitals can be transformed to the so-called localized MOs by a unitary transformation which makes $|\Psi_{HF}\rangle$ defined in Eq. (3) invariant. However, the coefficients of the other terms in CISD ground state (5) do not remain the same after this transformation. Hence, the orbital correlations strongly depend on the MOs under consideration. This seems reasonable as a unitary transformation preserves the global properties such as total energy, but not the subsystem structure and the resulting local properties.

For the open shell molecules, there is an ambiguity in the definition of MOs as two-mode subsystems even in the absence of any transformation. This arises from the fact that the unrestricted HF method allows the α and β modes to have different energies even if they share the same symmetry, i.e., if they can be written as almost the same superposition state in the basis of atomic orbitals. In some molecules such as C$_2^-$, the situation becomes more complicated. The modes sharing the same symmetry may appear in different orders when the α and β modes are ordered separately according to their energies. But how would orbital correlations alter if two-mode subsystems were defined by symmetry similarity rather than the energy ordering?

Let us reconsider the orbitals 5, 6, and 7 that do not share any quantum correlation with the other MOs in the dicarbon anion. Assume we redefine these three two-mode subsystems by combining the constituent α and β modes with the same symmetry. In this case, the resulting orbitals become strongly correlated with the rest as shown in Fig. 4. As a matter of fact, they are equal to the 5th 1π$_u$ orbital, 6th 1π$_u$ orbital, and 7th 3σ$_g$ orbital in the neutral dicarbon molecule. Then it is not clear which orbital definition would be more appropriate to understand what happens to correlations in the transition from the neutral to the anionic state of the molecule. In this respect, we are planning to extend the present methodology to investigate the dynamical nature of orbital correlations during
chemical processes.

Although the electronic structure of molecules and many of their observed properties are fairly well described by HF MOs, it should be emphasized that they represent an approximation to reality. If we could solve the electronic Schrödinger equations exactly without any approximation, we would get “real” molecular ground states. However, these states would still be superpositions in the bases that describe the individual atoms. That is, it would still be possible, at least in principle, to find classical and quantum correlations in the ground states of molecules.

Finally, we would also stress that the local SSRs increase the entropy of molecular electronic states while removing some part of their classical and quantum correlations. For example, the entropy of the water molecule is risen in its ground state approximately by 0.13 and 0.31 after P-SSR and N-SSR, respectively. The same values are 0.76 and 0.84 for the dicarbon anion. Thus, although some orbital correlations become inaccessible in the presence of SSRs, the entropic cost of this inaccessibility can reduce the free energy of the molecules. Even the orbital correlations frozen by SSRs can become important for the quantum information processing tasks indirectly in this way. Moreover, these frozen correlations can be also unlocked by transferring them either to a different set of fermionic modes or to an entirely different system by means of global operations. However, the possible resource values of the orbital correlations frozen by local SSRs are beyond the scope of this methodological paper, though their investigation is a natural direction to pursue future work.

V. CONCLUSION

In the present work, we have analyzed the electronic ground states of three prototypical molecules, namely H2O, C2H6, and C3H5, using the tools of fermionic information theory that is still an active research area.

Although the α and β modes are two-level distinguishable quantum systems, the map of molecular electronic states into multipartite qubit states leads to some ambiguities in defining the subsystems. Therefore, we have applied the fermionic partial trace operation to obtain the single- and double-orbital states. We have further taken into account the additional constraints that the local (parity and number) superselection rules put on the spaces in which these reduced states live. In particular, we have found that the computational complexity of orbital discord is significantly lower when compared to the four-qubit quantum discord. This enables us to explicitly discuss both the classical and quantum parts of the pairwise orbital correlations in the presence of superselection rules.

Remarkably, we have observed that quantum orbital correlations can dominate the total orbital correlations and survive even in the absence of orbital entanglement. We have also examined whether the symmetries of the constituent orbitals make a difference in terms of correlations. Besides, when the orbital density matrices are treated as qubit states, we have shown that orbital entanglement would be underestimated.

We believe our work can serve the needs of future investigations in understanding the nature of the correlations in chemical systems.

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[1] F. A. Weinhold, Chemical Bonding as a Superposition Phenomenon, J. Chem. Educ. 76, 1141 (1999).
[2] L. Pauling, The nature of the chemical bond and the structure of molecules and crystals., 3rd ed. (Cornell University Press, 1960).
[3] C. A. Coulson, Valence, 1st ed. (Oxford University Press, 1952).
[4] P. C. Hiberty and C. Leforestier, Expansion of molecular orbital wave functions into valence bond wave functions. a simplified procedure, J. Am. Chem. Soc. 49, 473001 (1978).
[5] S. Shaik, D. Danovich, and P. C. Hiberty, Valence bond theory— its birth, struggles with molecular orbital theory, its present state and future prospects, Molecules 26, 1624 (2021).
[6] A. G. J. MacFarlane, J. P. Dowling, and G. J. Milburn, Quantum technology: the second quantum revolution, Phil. Trans. R. Soc. Lond. A 361, 1655 (2003).
[7] K. Modi, A. Brodutch, H. Cable, T. Paterek, and V. Vedral, The classical-quantum boundary for correlations: Discord and related measures, Rev. Mod. Phys. 84, 1655 (2012).
[8] G. Adesso, T. R. Bromley, and M. Cianciaruso, Measures and applications of quantum correlations, J. Phys. A: Math. Theor. 49, 473001 (2016).
[9] R. Horodecki, P. Horodecki, M. Horodecki, and K. Horodecki, Quantum entanglement, Rev. Mod. Phys. 81, 865 (2009).
[10] M. D. Reid, P. D. Drummond, W. P. Bowen, E. G. Cavalcanti, P. K. Lam, H. A. Bachor, U. L. Andersen, and G. Leuchs, Colloquium: The Einstein-Podolsky-Rosen paradox: From concepts to applications, Rev. Mod. Phys. 81, 1727 (2009).
[11] L. Pezzè, A. Smerzi, M. K. Oberthaler, R. Schmied, and P. Treutlein, Quantum metrology with nonclassical states of atomic ensembles, Rev. Mod. Phys. 90, 035005 (2018).
[12] L. Henderson and V. Vedral, Classical, quantum and total correlations, J. Phys. A: Math. Gen. 34, 6899 (2001).
[13] H. Olliver and W. H. Zurek, Quantum discord: A measure of the quantumness of correlations, Phys. Rev. Lett. 88, 017901 (2001).
[14] T. Werlang and G. Rigolin, Thermal and magnetic quantum discord in Heisenberg models, Phys. Rev. A 81, 044101 (2010).
[15] R. Dillenschneider, Quantum discord and quantum phase transition in spin chains, Phys. Rev. B 78, 224413 (2008).
[16] B. Dakić, Y. O. Lipp, X. Ma, M. Ringbauer, S. Kropatschek, S. Barz, T. Paterek, V. Vedral, A. Zeilinger, Č. Bukner, and
Opt. Meth. Softw. 11, 545 (1999).

[59] R. H. Tütüncü, K. C. Toh, and M. J. Todd, Solving semidefinite-quadratic-linear programs using SDPT3, Math. Program., Ser. B 95, 189 (2003).