

Foundations of Quantum Information for Physical Chemistry

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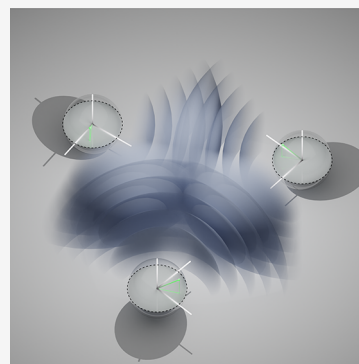
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ABSTRACT: Quantum information, a field in which great advances have been made in the past decades, now presents opportunities for advanced chemistry. One roadblock to progress, especially for experimental chemical science, is that new concepts and technical definitions need to be learned. In this paper, we review some basic, but sometimes misunderstood, concepts of quantum information based on the mathematical formulation of quantum mechanics that will be useful for chemists interested in discovering ways that chemistry can contribute to the quantum information field. We cover topics including qubits and their density matrix formalism, quantum measurement as a quantum operation, information theory, and entanglement. We focus on the difference between the concepts in the quantum context and the classic context. We also discuss the relation and distinction among entanglement, correlation, and coherence. We aim to clarify the rigorous definition of these concepts and then indicate some examples in physical chemistry.



Quantum information, which has become especially prominent in the past decade, demonstrated the potential for new kinds of technology relevant to information processing, communications, and sensors in the framework of quantum mechanics.¹ These new ways of handling information are based on exploiting special correlations encoded in quantum states that serve as resources. The field began with the study of nontrivial quantum phenomenon in cold atoms and quantum optics,² and now researchers are also interested in detecting nontrivial quantum phenomena in chemical molecules.³ Owing to their small size and fundamentally quantum-mechanical nature, molecules may provide interesting building blocks for quantum resources.⁴ We already know of fundamental examples, particularly based on electron and nuclear spin states. The next challenge is to put quantum correlations to work to produce new kinds of chemical-scale functions.⁵

With the development of ultrafast spectroscopy that can prepare superpositions and resolve the evolution of superposition states known as wavepackets, coherence phenomena in molecular and biological systems are drawing more attention from the chemistry community. The field opens many fundamental questions such as how to identify functions that arise from underlying nonclassical dynamics. More recently still, there has been interest in working out how chemical systems will be useful for quantum information and related technologies.⁶ To elucidate these opportunities, it is important to appreciate fundamentally what constitutes quantum resources. It is also an open challenge to describe and identify quantum correlations in complex molecular systems. There are many challenges to address at the intersection of molecules and quantum information in chemistry. Questions of interest

include: How do we design molecules that have quantum states serving demonstrably as a resource that enables a quantum function? How do we maintain molecular quantum states with long coherence time against a noisy environment? How do we think about unique quantum resources enabled by chemical systems, but not hidden by the inherent complexity of those systems? Ways of addressing these kinds of problems might be inspired by a physical understanding of the basis of quantum information.

Our aim in this paper is to provide a rigorous, but succinct, background of the quantum information field relevant to researchers in physical chemistry. We have tried to use terminology and examples familiar to this target readership. The paper is particularly relevant for spectroscopy and dynamics in physical chemistry, where quantum phenomena such as quantum coherence are of current interest. We will briefly review how to describe quantum states as density matrices, how to control quantum systems via measurement, and how to understand their important features, including entanglement and entropy. We will clarify the relation between the concepts of quantum entanglement, quantum correlation, and quantum coherence. We will focus on the potential advantages of quantum systems that differentiate quantum entanglement and quantum information from classical correlation and classical information. Some examples of

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chemical systems are provided throughout to illustrate the utility of quantum information principles in a molecular chemistry context.^{7–11}

■ QUBITS AND SUPERPOSITION

Classical protocols for digital communication and computation are based on bits, like switches that can toggle between 0 and 1 positions. A system of n classical switches can encode 2^n different classical states, that is, unique configurations of the switches, e.g. 01110010...

The classical state can be directly generalized to a quantum state, where each switch is replaced by a two-level quantum system, such as a spin-half electron or a single-excitation molecular exciton, known as quantum bits, or qubits. The quantum state of a sequence of n qubits in the orthonormal basis of $|0\rangle$ and $|1\rangle$ can be constructed from the tensor product, like $|0\rangle|1\rangle|1\rangle|1\rangle|0\rangle|0\rangle|1\rangle|0\rangle...$. In total, we obtain 2^n unique product states in Hilbert space $\mathcal{H}$, very much like the classical sequence of switches. This set of product states forms one possible basis for $\mathcal{H}$.

A critical feature that distinguishes the qubits from classical bits is quantum superposition, which is similar to wave interference when added in or out of phase. A qubit may not be on either $|0\rangle$ or $|1\rangle$ but instead in a coherent superposition state,¹² represented by a wave function $|\psi\rangle = c_0|0\rangle + c_1|1\rangle$, where c_0 and c_1 are complex numbers satisfying the normalization condition $|c_0|^2 + |c_1|^2 = 1$. Without loss of generality, we can take $c_0 = \cos \frac{\theta}{2}$, $c_1 = \sin \frac{\theta}{2} e^{i\phi}$, where θ and ϕ are in the range $0 \leq \theta \leq \pi$ and $0 \leq \phi < 2\pi$, respectively. Here, we drop the global phase between $|0\rangle$ and $|1\rangle$ because it has no observable effects, and ϕ is the relative phase between $|0\rangle$ and $|1\rangle$. The physical meaning of θ and ϕ can be interpreted as the polar angle and the azimuth angle of spherical polar coordinates, which together represent the points on a unit sphere, known as the Bloch sphere. The details of the Bloch sphere are discussed in the next section, as summarized in Figure 2. The wave function of a qubit can be bijectively mapped (one-to-one correspondence) to a unit vector $\vec{n}$ with the spherical polar direction (θ, ϕ)

$$|\psi\rangle = |\vec{n}\rangle = \cos \frac{\theta}{2} |0\rangle + \sin \frac{\theta}{2} e^{i\phi} |1\rangle \quad (1)$$

The wave function of a qubit can be expressed by only two real numbers, a unit vector, instead of two complex numbers.

This wave function formalism is essential to account for the phase relationships underlying quantum superposition, or more rigorously, quantum coherence between $|0\rangle$ and $|1\rangle$. Consider the expectation value of an observable O in the state $|\psi\rangle$

$$\begin{aligned} \langle O \rangle = \langle \psi | O | \psi \rangle &= |c_0|^2 \langle 0 | O | 0 \rangle + |c_1|^2 \langle 1 | O | 1 \rangle + c_0 c_1^* \langle 1 | O | 0 \rangle \\ &+ c_1 c_0^* \langle 0 | O | 1 \rangle \end{aligned} \quad (2)$$

The last two terms on the RHS of eq 2 represent the effect of superposition, which might be either constructive or destructive, while in a classical system, we interpret $\langle O \rangle$ as the classical probability that our system has property O , and the expression is solely comprised of the first two terms in eq 2. Thus, superposition is a unique feature of quantum systems. Quantum coherence between $|0\rangle$ and $|1\rangle$ then can be defined by $c_0 c_1^*$, or its complex conjugate $c_1 c_0^*$, to quantify the magnitude of superposition. The superposition can be easily

generalized to n qubits in $\mathcal{H}$. Some famous examples of the qubit superposition states are the Bell states

$$|\Psi_{\pm}\rangle_{AB} = \frac{1}{\sqrt{2}} (|0\rangle_A \otimes |1\rangle_B \pm |1\rangle_A \otimes |0\rangle_B) \quad (3a)$$

$$|\Phi_{\pm}\rangle_{AB} = \frac{1}{\sqrt{2}} (|0\rangle_A \otimes |0\rangle_B \pm |1\rangle_A \otimes |1\rangle_B) \quad (3b)$$

where subscripts A and B label the two qubits and AB labels the composite system. Bell states form an orthonormal basis. Bell states are famous examples of quantum entanglement, which will be discussed in the following sections.

■ DENSITY MATRIX FORMALISM

Previously we only discussed pure states in the wave function formalism. Pure states of practical interest provide an excellent foundation for understanding but tend to be fragile in molecular systems. A general way to describe qubits and other quantum systems is the density matrix formalism.¹³

Mixed State. The idea of mixed states originates from statistical ensembles, where the states of the quantum system are not completely known but obey certain statistical distributions. Statistical ensembles are virtual copies of a real system, and each virtual system represents a possible state $|\psi_i\rangle$. Statistically, the real system can be in the state $|\psi_i\rangle$ with the probability p_i (satisfying $p_i \geq 0$ and $\sum_i p_i = 1$). The set $\{p_i, |\psi_i\rangle\}$ is known as an ensemble of pure states,⁷ or a mixed state. Particularly, in the uniform ensemble $\{1, |\psi\rangle\}$ where all the virtual systems are in the same quantum state, this system can be simply described by the pure state $|\psi\rangle$.

The ensemble of pure states $\{p_i, |\psi_i\rangle\}$ can be further written as a density matrix

$$\rho = \sum_i p_i |\psi_i\rangle \langle \psi_i| \quad (4)$$

Eq 4 shows that the state representing the ensemble will be a statistical mixture of pure states. In particular, a uniform ensemble, i.e. a pure state $|\psi\rangle$ can be similarly expressed in the density matrix formalism as

$$\rho = |\psi\rangle \langle \psi| \quad (5)$$

The redundant global phase is eliminated in the density matrix formalism, and only the necessary relative phase in eq 1 counts. Thus, density matrices are the more general and concise expression of quantum states. The expectation value of an operator O in a state ρ , i.e., the average of $\langle \psi_i | O | \psi_i \rangle$, is

$$\langle O \rangle = \sum_i p_i \langle \psi_i | O | \psi_i \rangle = \text{Tr}(O\rho) \quad (6)$$

Notice that each $|\psi_i\rangle$ in eq 4 does not need to be orthogonal to others. Thus, $\{p_i, |\psi_i\rangle\}$ in eq 4 is not the set of eigenvalues and eigenstates of ρ , and the definition of a density matrix (eq 4) is not the eigendecomposition of ρ . One may also diagonalize the density matrix

$$\rho = \sum_{m=1}^N \lambda_m |m\rangle \langle m| \quad (7)$$

where $|m\rangle$ is an orthonormal basis in the Hilbert space and $N = \dim(\rho)$ is the dimension of this Hilbert space. In this paper, we denote λ_m as the eigenvalue of the density matrix and $\{p_i\}$ as a set of probabilities. One can deduce that the eigenvalues of ρ

satisfy $\lambda_m \geq 0$ and $\sum_{m=1}^N \lambda_m = 1$. Thus, $\{\lambda_m\}$ is also a set of probabilities.

The density matrix is Hermitian ($\rho = \rho^\dagger$), positive semidefinite ($\langle \psi | \rho | \psi \rangle \geq 0$ for any given $|\psi\rangle$), and of unit trace ($\text{Tr}(\rho) = 1$).¹⁴ Generally, any operator satisfying these three conditions is a density matrix. The set comprising all the density matrices of a certain dimension is called the Liouville space, which is a space of bounded operators on Hilbert space. Liouville space is a convex set,⁷ which means that a convex combination of some density matrices is still a density matrix in Liouville space, i.e., $\rho = \sum_i p_i \rho_i$ with $p_i \geq 0$ and $\sum_i p_i = 1$, known as the incoherent superposition. Pure states cannot be a convex combination of other states in Liouville space, so they comprise the convex hull of Liouville space¹⁵ (Figure 1). This point turns out to be extremely important for quantum information because entanglement (and other quantum correlations) are hidden and diluted in mixed states.

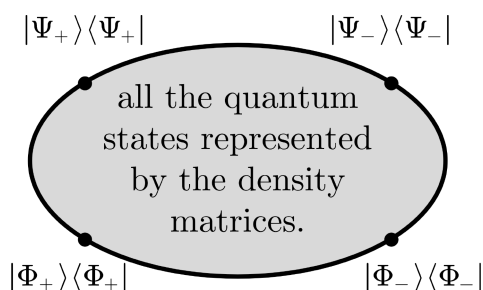


Figure 1. Illustration for convexity of Liouville space. All pure states (the black solid curve) comprise the convex hull for the Liouville space of all the density matrices. These pure states include the Bell states, shown schematically, in the example.

Purity. Even though the definition of a density matrix (eq 4) may not be its eigendecomposition, the special case of the pure state (eq 5) always is. By comparing eqs 5 and 7, we can see that the density matrix is pure if and only if it has only one nonzero eigenvalue. This is the criterion for a pure state. Moreover, we can define the purity of a density matrix to quantify mixedness:

$$\gamma(\rho) = \text{Tr}(\rho^2) = \langle \rho \rangle \quad (8)$$

Purity is a useful gauge of the mixedness of states in the Liouville space. A more mixed system has a lower purity.

Equation 8 means that purity is the expectation value of the density operator. A more uniformly distributed density operator generates a smaller expectation value.

A density matrix ρ is a pure state if and only if $\gamma(\rho) = 1$, and otherwise $\frac{1}{N} \leq \gamma(\rho) < 1$ for mixed states, where $N = \dim(\rho)$ is the dimension of ρ . To prove this, one can diagonalize the density matrix (eq 7) to calculate $\text{Tr}(\rho^2) = \sum_{m=1}^N \lambda_m^2$. Because $0 \leq \lambda_m \leq 1$, one has $\lambda_m^2 \leq \lambda_m$. Therefore, $\gamma(\rho) = \sum_{m=1}^N \lambda_m^2 \leq \sum_{m=1}^N \lambda_m = 1$. The equality condition is satisfied when $\lambda_m^2 = \lambda_m$, i.e., $\lambda_m = 0, 1$. Due to the unit trace condition $\sum_{m=1}^N \lambda_m = 1$, only the pure state has the purity of 1. The lower bound of $\gamma(\rho)$ can be proven by the Cauchy–Schwarz inequality: $(\sum_{m=1}^N \lambda_m \times 1)^2 \leq (\sum_{m=1}^N \lambda_m^2)(\sum_{m=1}^N 1^2)$, which ends up with $\frac{1}{N} \leq \gamma(\rho)$. The equality condition for the lower bound is $\lambda_m = \frac{1}{N}$, i.e., $\rho = \frac{1}{N}I$. The normalized identical operator refers to a completely mixed state, where each eigenstate contributes the same probability.

Purity has many applications in chemistry. For example, in a molecular aggregate system, a widely used tool to describe the molecular exciton delocalization¹⁶ is inverse participation ratio (IPR),^{17,18} defined as the second moment of the probability density:

$$\text{IPR} = \sum_x |\langle x | \psi \rangle|^4 \quad (9)$$

where $|\psi\rangle$ is the exciton state and x labels the site of a localized exciton. An exciton state with a smaller IPR implies more delocalization. IPR is the purity of the state after projection-valued measurement (PVM, see eq 14), $\text{IPR} = \gamma(\rho')$, which means delocalization can be described by postmeasurement purity.

Bloch Sphere. Now we can generalize eq 1 to describe a single qubit beyond the pure state in the density matrix formalism, i.e., a two-dimensional density matrix ρ . It is easy to prove that it can always be decomposed as

$$\rho = \frac{1}{2}(I + \vec{r} \cdot \vec{\sigma}) = \frac{1}{2}(I + r_x \sigma_x + r_y \sigma_y + r_z \sigma_z) \quad (10)$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the Pauli vector with the three components being the Pauli matrices. $\vec{r}$ is known as the Bloch vector. The length of the Bloch vector $r = |\vec{r}|$ is in the range $0 \leq r \leq 1$ to satisfy the positive semidefinite condition. The Bloch vector can be explicitly calculated by

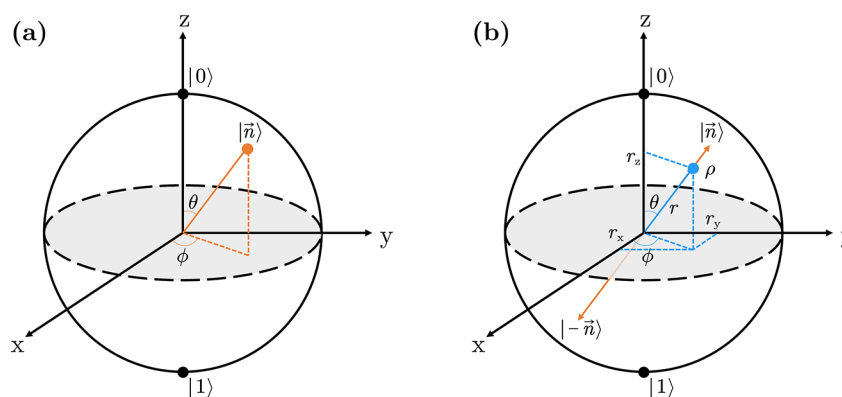


Figure 2. Illustration of Bloch sphere. (a) Any pure state $|\psi\rangle$ (orange) on Bloch sphere can be represented by a unit vector $\vec{n}$, in (θ, ϕ) coordinates. (b) Any mixed state ρ (blue) inside Bloch sphere can be represented by a Bloch vector $\vec{r}$ in (r_x, r_y, r_z) or (r, θ, ϕ) coordinates, whose eigenvectors are $|\vec{n}\rangle$ and $|\vec{n}\rangle$.

$$\vec{r} = (r_x, r_y, r_z) = \text{Tr}(\vec{\sigma}\rho) \quad (11)$$

where each component is $r_\alpha = \text{Tr}(\sigma_\alpha \rho)$, owing to the relation $\text{Tr}(\sigma_\alpha \sigma_\beta) = 2\delta_{\alpha\beta}$, $\alpha, \beta = x, y, z$. Generally, the Pauli matrices together with the identity operator, $\{I, \sigma_x, \sigma_y, \sigma_z\}$, form a complete orthonormal basis spanning the single-qubit Liouville space when the inner product is defined as $\langle \rho_1, \rho_2 \rangle = \frac{1}{2} \text{Tr}(\rho_1^\dagger \rho_2)$. Thus, there exists a one-to-one correspondence between a single-qubit state and a Bloch vector (eq 10), i.e., a bijection mapping from ρ to $\vec{r}$. Considering $0 \leq r \leq 1$, Bloch vectors are the points inside or on the surface of a unit sphere, the Bloch sphere, as shown in Figure 2.

The vector length r of the Bloch vector is an indicator for the mixedness of single-qubit states. To see this, one can calculate the purity of ρ

$$\gamma(\rho) = \frac{1 + r^2}{2} \quad (12)$$

When $r = 1$, $\gamma(\rho) = 1$, ρ is a pure state. When $0 \leq r < 1$, $\frac{1}{2} \leq \gamma(\rho) < 1$, ρ is a mixed state. When $r = 0$, $\gamma(\rho) = \frac{1}{2}$, ρ is a completely mixed state. Thus, Bloch vectors on the Bloch sphere represent the pure states, while inside the Bloch sphere, they represent the mixed states. The closer a state is to the center of the Bloch sphere, the more mixed it is.

It is also convenient to transform Bloch vectors from Cartesian coordinates to a spherical coordinate system $\vec{r} = (r_x, r_y, r_z) = (r, \theta, \phi)$, where $r_x = r \sin \theta \cos \phi$, $r_y = r \sin \theta \sin \phi$, $r_z = r \cos \theta$. In the special case of a pure state ($r = 1$), we can find the corresponding state $\rho = \frac{1}{2}(I + \vec{n} \cdot \vec{\sigma}) = |\vec{n}\rangle\langle\vec{n}|$, where $\vec{n} = \vec{r}$ and $|\vec{n}\rangle$ is defined as eq 1. The polar angle and azimuthal angle in eq 1 are the same as (θ, ϕ) in this section. The wave function formalism for a single qubit can be recovered from the density matrix formalism with a Bloch sphere. Generally, given any Bloch vector in the spherical coordinate system, one can diagonalize ρ

$$\rho = \frac{1+r}{2} |\vec{n}\rangle\langle\vec{n}| + \frac{1-r}{2} |-\vec{n}\rangle\langle-\vec{n}| \quad (13)$$

where $\vec{n} = \frac{\vec{r}}{r}$ is the unit vector with the same direction (θ, ϕ) as the Bloch vector $\vec{r}$ and $-\vec{n}$ is in the opposite direction. $|\vec{n}\rangle$ and $|-\vec{n}\rangle$ are orthogonal to each other: $\langle\vec{n}|\vec{n}\rangle = 0$.

The Bloch sphere provides a useful means of visualizing the state of a single qubit and often serves as an excellent test bed for ideas about quantum information.⁷ The quantum dynamics of a single qubit can be mapped to the dynamics of a Bloch vector. For example, unitary evolution fixes the Bloch vector on a sphere because r is invariant. In the orthonormal basis of $|0\rangle$ and $|1\rangle$, dephasing means the decrease of r_x and r_y , while decay from $|1\rangle$ to $|0\rangle$ means the increase of r_z . For multiple qubits, if we are only interested in the coherent spin state or spin squeezing,^{19,20} the Bloch sphere is also a useful tool. However, a general description for N -qubits is limited because the general Bloch sphere lies in a $(4^N - 1)$ -dimension space.

■ QUANTUM MEASUREMENT

In experiments, we perform measurements by interacting the system of interest with the measuring apparatus and getting a sequence of outcomes from the apparatus. In the case of a classical system, our ensemble yields properties of the probability distribution with respect to an appropriate random

variable. It is reasonable to believe that the measurement apparatus only interacts with the system with a negligible perturbation and therefore does not irreversibly change the observed system. This feature for classical systems is called realism.²¹

The challenge for measurements on quantum systems is to construct an analogous map from the set of states to a probability distribution²² such that we account for the quantum phase encoded in superposition and quantum coherence. A closed quantum system, which ideally does not interact with the rest of the world, evolves according to unitary evolution, without losing quantum coherence. However, when the measuring apparatus, an external system, observes the system to obtain the information inside the system, the interaction makes the system open. Thus, measurement involves a nonunitary evolution of the system, which may destroy the fragile quantum coherence. One may think about studying a large and isolated composite system, the observed system together with the external system, which again obeys unitary evolution. But in practice, it is hard to handle such a closed system because usually we know little about the environment and a large system means an exponential increase in mathematical complexity. So we need other ways to describe the system locally when measuring it, which is called quantum measurement theory. Quantum measurement theory is sometimes considered one of the fundamental postulates of quantum mechanics.⁷

Projective Measurements and PVM. The most typical example of quantum measurement theory is the wave function collapse theory. When we measure the system with an observable M (in the eigenbasis $|m\rangle$ of M), the wave function $|\psi\rangle$ will randomly collapse to a certain $|m\rangle$ with probability $|\langle m|\psi\rangle|^2$ and observation value ϵ_m . From the view of the ensemble, after the measurement we obtain a density matrix $\rho' = \sum_m |\langle m|\psi\rangle|^2 |m\rangle\langle m|$, and the expectation value of M is $\langle M \rangle = \sum_m |\langle m|\psi\rangle|^2 \epsilon_m$.

Generally, given a system prepared initially in a pure state $|\psi\rangle$, one can carry out the projective measurement with a series of projection operators $\{P_m\}$, which are Hermitian ($P_m^\dagger = P_m$), orthogonal ($P_m P_{m'} = \delta_{m,m'} P_m$), and complete ($\sum_m P_m = I$). The measurement operators satisfying these three conditions are also called projection-valued measure (PVM). Projective measurement aims to project $|\psi\rangle$ from Hilbert space $\mathcal{H}$ to the subspaces $\mathcal{H}_m$. Completeness insures $\mathcal{H} = \bigoplus_m \mathcal{H}_m$. After the measurement, the probability that the result m occurs is $p_m = \langle \psi | P_m | \psi \rangle$ and the corresponding quantum state is $\frac{P_m |\psi\rangle}{\sqrt{\langle \psi | P_m | \psi \rangle}}$. A

mixed state is generated from a pure state by PVM with the density matrix

$$|\psi\rangle \xrightarrow{\text{PVM}} \rho' = \sum_m P_m |\psi\rangle\langle\psi| P_m \quad (14)$$

PVM can be understood by the wave function collapse theory with an observable, M . P_m is chosen to be the spectral decomposition: $M = \sum_m \epsilon_m P_m$. The spectral theorem²³ guarantees Hermiticity, orthogonality, and completeness. This is a process of PVM where we take $P_m = |m\rangle\langle m|$. Operator M is so special because PVM does not change the expectation value of M , since $\langle \psi | M | \psi \rangle = \text{Tr}(M \rho')$.

PVM is very useful because most physical systems can only be measured in a very coarse manner. PVM has a property known as repeatability,⁷ which means if we perform a PVM

once and obtain the outcome m , repeating the same PVM immediately gives the outcome m again and does not change the state. Repeatability originates from the orthogonality of PVM operators, which is not guaranteed for many other quantum measurements. To solve this problem, we need a more universal protocol for quantum measurement, known as general measurement.

General Measurement and POVM. General measurement provides a perspective to prepare a mixed state ρ' from a pure state. Similar to the repeated test in the laboratory, by preparing an infinite number of copies of the initial pure state $|\psi\rangle$ and doing the same measurement on each copy, we can summarize all the possible outcomes (labeled by m) and the corresponding probability p_m . We then have $\rho' = \sum_m p_m |\psi_m\rangle\langle\psi_m|$, which matches the definition of density matrix eq 4. This means that a general measurement of a pure state generates a mixed state. So we say general measurement is an equivalent way to define the density matrix of a mixed state, i.e., the ensemble of postmeasurement states. This procedure works intuitively because the structure of the mixed state reflects the probability distribution of the postmeasurement states. Sometimes the measurement may probe a specific spectral window or interval, so then we only include those states whose expectation values lie in that window and keep the other states with zero probability. Same as eq 4, postmeasurement states $|\psi_m\rangle$ do not have to be orthogonal to each other. This feature distinguishes general measurement from projective measurement.

Rigorously, general measurement is described by a set of measurement operators $\{M_m\}$ that satisfy completeness $\sum_m M_m^\dagger M_m = I$. These are operators, which do not have to be Hermitian, in the state space of the system being measured. Each outcome m (also known as quantum channel m) occurs with a probability

$$p_m = \langle\psi|M_m^\dagger M_m|\psi\rangle \quad (15)$$

and results in the quantum state

$$|\psi_m\rangle = \frac{M_m|\psi\rangle}{\sqrt{\langle\psi|M_m^\dagger M_m|\psi\rangle}} \quad (16)$$

The density matrix after general measurement can be written as

$$|\psi\rangle \xrightarrow{\text{POVM}} \rho' = \sum_m M_m|\psi\rangle\langle\psi|M_m^\dagger \quad (17)$$

Here general measurement is represented by “POVM”, whose meaning will be discussed later.

If additional conditions of Hermiticity ($M_m^\dagger = M_m$) and orthogonality ($M_m^\dagger M_{m'} = \delta_{m,m'} M_m$) are imposed on general measurement, we recover PVM. So PVM is a special case of general measurement. Moreover, PVM on a composite system augmented by unitary operations turns out to be completely equivalent to general measurements on subsystems.⁷

Sometimes, the postmeasurement state of the system eq 16 is of little interest, and we care more about the probabilities of the respective measurement outcomes because many statistical properties only depend on the probabilities. In this case, we can rewrite general measurement as $F_m = M_m^\dagger M_m$, so that the probability is

$$p_m = \langle\psi|F_m|\psi\rangle \quad (18)$$

The set of operators $\{F_m\}$ is known as positive operator-valued measure (POVM), which is sufficient to determine the probabilities of the different measurement outcomes. To avoid any confusion, in this paper, “positive” means “positive semidefinite”. Rigorously, the definition of POVM is a set of operators $\{F_m\}$ that is positive semidefinite ($\langle\phi|F_m|\phi\rangle \geq 0$) and complete ($\sum_m F_m = I$). POVM is simple and intuitive when only the measurement statistics matter. If the postmeasurement states are needed, one can always decompose F_m to recover M_m by $F_m = M_m^\dagger M_m$. PVM is also a special case of POVM where $F_m = M_m$.

If the initial state is prepared in a mixed state, eqs 15–17 can be generalized to

$$p_m = \text{Tr}(M_m \rho M_m^\dagger) = \text{Tr}(\rho F_m) \quad (19)$$

$$\rho_m = \frac{M_m \rho M_m^\dagger}{\text{Tr}(M_m \rho M_m^\dagger)} \quad (20)$$

$$\rho \xrightarrow{\text{POVM}} \rho' = \sum_m p_m \rho_m = \sum_m M_m \rho M_m^\dagger \quad (21)$$

In quantum operation, eq 21 is known as Kraus representation.²⁴

Measurement is an important part of quantum information.^{22,25,26} In addition to describing measurements of discrete quantum variables (systems with discrete spectra),²⁷ PVM and POVM can be extended to account for continuous measurement.^{28,29} A theory for continuous measurement is needed when we must account for the time it takes to complete the measuring process.

INFORMATION THEORY AND ENTROPY

In this section, we will discuss how to understand the information in a quantum system, compared to an analogous classical system. For example, n classical bits can encode 2^n distinct binary numbers, which is the same as the dimension of the Hilbert Space for n qubits. The maximum information encoded in either case is the same. However, the quantum advantage for conveying information comes from using compression strategies that are only available to quantum systems. To start, we need to define the amount of information,^{30,31} and we do so using entropy.

Classical Information and Shannon Entropy. Quantification of classical information was devised by Claude Shannon³² as an analogy to Gibbs entropy, known as Shannon entropy. Given a discrete random variable X with its probability distribution function $p(x)$, the Shannon entropy is defined as

$$H(X) = H(\{p(x)\}) = -\sum_x p(x) \ln p(x) \quad (22)$$

Intuitively, the amount of information we obtain from the occurrence of a certain event X is $-\ln p(X)$. The total Shannon entropy can then be understood as the average amount of information for measuring this random variable: $H(X) = E[-\ln p(X)]$. Shannon entropy only depends on the probability distribution. Shannon entropy is defined in this way to ensure that the total information learned from independent events is the sum of the information learned from each event:

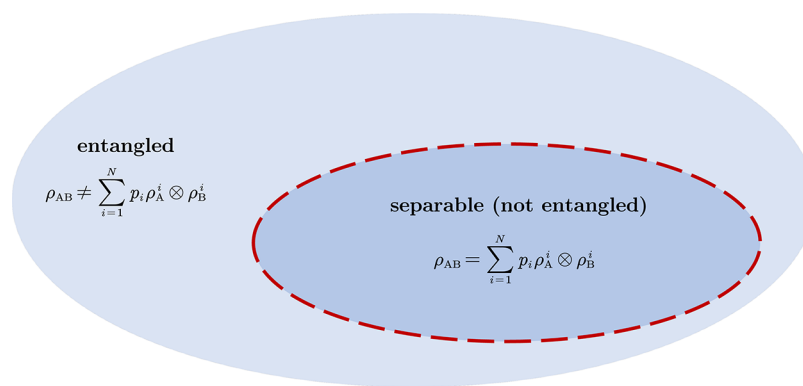


Figure 3. A set of all the bipartite states (Liouville space) as an illustration for entanglement and witness. The red dashed curve is the boundary between entangled states and separable states. The ellipses imply the convexity of the sets.

$$\begin{aligned} H(\{p_{X,Y}(x, y) = p_X(x)p_Y(y)\}) \\ = H(\{p_X(x)\}) + H(\{p_Y(y)\}) \end{aligned} \quad (23)$$

We can view the entropy either as a measure of our uncertainty before we learn the value of X , or as a measure of how much information we have gained after we learn the value of X .⁷ To understand this, we can ask a question: when transmitting information in a message (e.g., by code, telephone, etc.), how much error—or uncertainty—can be tolerated? For example [sic], can I get my message across sufficiently clearly if every “a” is erroneously transmitted as “x”? Obviously, this error is not catastrophic because we use the information provided by the other letters together with our knowledge about words in the English language, and possibly other information gathered by experience, to interpret the message correctly. We can explain this concept more rigorously with the following scenario.

In the next examples, we are going to think about searching for particular pairs of letters on a random page of an English text. Suppose that we are interested only in two letters in our document, “Q” and “T”. We scan through the words until we find either “Q” or “T”. The question is, how much information does identifying the letter give us? To answer that, we can normalize the probabilities for the events of finding “Q” and finding “T” as $p(Q) = 0.01$ and $p(T) = 0.99$. Because $p(T) \gg p(Q)$, the first “Q” or “T” we find will almost certainly be “T”. Thus, one measurement resulting in “T” provides very little information because it is unlikely to change our expectations, where the amount of information we gain from this measurement is $-\ln p(T) = 0.010$. However, one measurement resulting in “Q” provides a lot of information, because a rare event occurs beyond our expectation, where the amount of information we gain from this measurement is $-\ln p(Q) = 4.605$. From a statistical perspective, the average information we gain from the measurement is $H(\{p(Q), p(T)\}) \approx 0.056$. The Shannon entropy in this example is quite small because, before any measurement, we anticipate getting “T”. In contrast, if we are interested in the letters “M” and “W”, the probability distribution for finding “M” and finding “W” will be $p(M) = 0.5$ and $p(W) = 0.5$. Now the measurement provides the most possible information because we really cannot guess whether the first “M” or “W” on the page will be “M” or “W”. The Shannon entropy is as large as $H(\{p(W), p(M)\}) \approx 0.69$.

Quantum Information and Von Neumann Entropy. Classical probability has its analogy in quantum mechanics as a

density matrix, where coherence is considered. Quantum information¹⁰ is quantified with respect to the density matrix of the quantum system via the von Neumann entropy:

$$S(\rho) = -\text{Tr}(\rho \ln \rho) = \langle -\ln \rho \rangle \quad (24)$$

Here we naturally replace the classical probability distribution in eq 22 by the density matrix. In statistical physics, taking ρ in eq 24 as a thermal ensemble, $\rho = \frac{1}{Z} e^{-H/k_B T}$, recovers Gibbs entropy. To calculate $S(\rho)$ practically, one may diagonalize ρ by eq 7 and have $S(\rho) = -\sum_{m=1}^N \lambda_m \ln \lambda_m$.

Different from the classical system, each measurement we do to the system will lead to a nonunitary evolution. So the postmeasurement will not perfectly recover the information carried by the initial density matrix. Suppose a PVM $\{P_m\}$ is performed on a quantum system ρ , but we never learn the result of the measurement. It can be proven that⁷

$$S(\rho') = S\left(\sum_m P_m \rho P_m\right) \geq S(\rho) \quad (25)$$

where the postmeasurement density matrix ρ' is defined by eq 14. The equality condition is reached if and only if $\rho' = \rho$, which means ρ is orthogonal in the basis of $\{P_m\}$. Notice that the PVM causes all of the off-diagonal entries of ρ to vanish while leaving the diagonal entries unchanged. Thus, the diagonal matrix ρ' is classical-like; that is, the diagonal elements of the ρ' can then be interpreted as classical probabilities. So $S(\rho')$ is the same as Shannon entropy $H(\{\text{Tr}(\rho P_m)\})$. This relation underlies an advantage for quantum information, whereby the information transfer capacity of a quantum system is constrained differently than that of a classical system.³³

While one qubit does not convey more information than one classical bit, the quantum correlations in an entangled system can be exploited to enable information to be more compressed. The idea is along the lines of superdense coding.⁷ A notable advantage of quantum information, therefore, is that quantum dense coding allows quantum communication channels to have greater capacity than comparable classical channels.^{34,35} A second advantage is that quantum mechanical laws can be leveraged to make communication more secure. Communications can be encrypted in new ways such that it is difficult for an eavesdropper to copy information, and quantum “keys” can be more difficult to crack.^{10,36,37}

■ QUANTUM ENTANGLEMENT

Entanglement is a central concept and key resource in quantum information. In this section, we will give a rigorous definition of quantum entanglement and discuss the possible ways to describe entanglement in different cases.

Separability. In quantum mechanics, the opposite of entanglement is separability,³⁸ which has features corresponding to classical correlation or even uncorrelatedness (see Figure 5). Separable states are the quantum states of a composite system that can be factorized into individual states belonging to separate subsystems. For example, a bipartite pure state is separable if it can be written as a product state

$$|\Psi\rangle = |\psi\rangle_A \otimes |\psi\rangle_B \quad (26)$$

More generally, a bipartite mixed state is separable if it can be decomposed into a sum of tensor products

$$\rho_{AB} = \sum_i p_i \rho_A^i \otimes \rho_B^i \quad (27)$$

where $p_i > 0$ and $\sum_i p_i = 1$. Without loss of generality, the separable mixed state can be equivalently defined based on separable pure states

$$\rho_{AB} = \sum_i q_i |\Psi^i\rangle_{AB} \langle \Psi^i|_{AB} \quad (28)$$

where $q_i > 0$ and $\sum_i q_i = 1$, and $|\Psi^i\rangle_{AB}$ are series of separable pure states. Equation 27 keeps the convexity of separable density matrices (any convex combination of separable density matrices is separable, as shown in Figure 3), and eq 28 shows that the pure product states (eq 26) comprise the convex hull of the separable set. The definition of separable states (eq 27) can be easily generalized to multipartite states by the tensor product of more subsystems.

Then we can give a rigorous mathematical definition of entanglement. A nonseparable quantum state is called an entangled state; that is, entangled states cannot be convexly decomposed as tensor product states:

$$\rho_{AB} \neq \sum_i p_i \rho_A^i \otimes \rho_B^i \quad (29)$$

The distinction between entanglement and separability is illustrated in Figure 3 by the dashed red curve. The convexity property does not hold for entangled states (Figure 3).

Separable states are important in quantum chemistry because they have classical and intuitive analogies. One example is the time-dependent Hamiltonian. Intuitively, a closed system can only be described by a time-independent Hamiltonian, so there must exist an external driving for the time-dependent Hamiltonian. When the system is classically driven, there is no entanglement between the system and the external driving, and thus, we can use the time-dependent Hamiltonian to quantumly study the dynamics of the system while treating the system-driving correlation classically. A similar example is the Markov approximation in the open quantum system approach, which is valid when the bath is disentangled from the system so that the bath loses its memory during the dynamics, such as Lindblad or Redfield dynamics.³⁹ However, the breakdown of the Markov approximation requires non-Markovian dynamics.⁴⁰

Another example of separable bipartite pure states comes from the Born–Oppenheimer (BO) approximation for electronic structure calculation. The molecule is treated as a

bipartite system (the electronic subsystem and the nuclear subsystem). We then use the Born–Oppenheimer approximation to assume that the nuclear degrees of freedom are at a fixed geometry R_0 , and thus, the total wave function is a product state of the electron wave function and the nuclear wave function: $|\Psi_{\text{en}}^{\text{BO}}(r, R)\rangle = |\psi_e(r; R_0)\rangle \otimes |\psi_n(R)\rangle$. Such a separable state is sometimes called a crude BO state,⁴¹ as we roughly assume that ψ_e is independent of R . The crude BO approach is valid when we are only interested in the static electronic energy at a certain geometry rather than the dynamics, or in the dynamics where the vibration is weak and nuclear geometry does not change too much (e.g., the nuclear coordinates are far away from the potential energy surface crossing).

However, in general, the Born–Oppenheimer approximation $\Psi_{\text{en}}(r, R) \approx \psi_e(r; R)\psi_n(R)$ can only give a less entangled state rather than a separable state because the “electronic wave function” $\psi_e(r; R)$ changes with the nuclear geometry R . More rigorously, the “electronic wave function” $\psi_e(r; R)$ is actually not the wave function of the electronic subsystem; it still lies in the total space containing both electrons and nuclei and carries electrons–nuclei entanglement. The BO approximation is a protocol to find a factorization $\psi_e(r; R)\psi_n(R)$ that matches the exact total wave function $\Psi_{\text{en}}(r, R)$, and this factorization often satisfies the weak (but non-zero) electron–nucleus entanglement in $\psi_e(r; R)$, which can thus be interpreted as the “electronic wave function”. Sometimes the electron–nuclear entanglement can even be strong in such BO approximation (e.g. the BO state is spanned by several crude BO states) because the entanglement of the BO state (distance measure to the crude BO state) and the accuracy of the BO approximation (distance measure to the exact state) are two different measures.⁴¹ Moreover, the breakdown of the Born–Oppenheimer approximation will lead to an entangled molecular state, which requires a more sophisticated treatment like non-adiabatic dynamics.⁴²

Schmidt Decomposition and Entanglement Entropy

Although the criterion of separability and quantifying entanglement of a general multipartite system or mixed state is an NP-hard problem (i.e., it cannot be solved in polynomial time with respect to the size of the system),⁴³ there is a rigorous and standard approach to quantifying entanglement of a bipartite pure state, based on Schmidt decomposition.

Schmidt decomposition⁴⁴ is valid if and only if the quantum state is bipartite and pure, which can always be decomposed into a sum of product states factorized by an orthonormal basis $|\alpha_n\rangle_A$ for subsystem A and an orthonormal basis $|\beta_n\rangle_B$ for subsystem B

$$|\Psi\rangle_{AB} = \sum_{n=1}^N \sqrt{\lambda_n} |\alpha_n\rangle_A \otimes |\beta_n\rangle_B \quad (30)$$

where the Schmidt coefficients $\sqrt{\lambda_n}$ are the non-negative numbers satisfying $\sum_{i=1}^N \lambda_i = 1$. The orthonormal bases $|\alpha_n\rangle_A$ and $|\beta_n\rangle_B$ are known as the Schmidt bases of subsystems A and B, respectively. The upper limit of the summation $N = \min\{N_A, N_B\}$ is defined by the smaller one between the dimension of system A and the dimension of system B.

By comparing eq 26 and eq 30, one can see that the separability criterion for a bipartite pure state is that only one of the Schmidt coefficients equals 1 and all the other Schmidt coefficients are 0. The number of nonzero Schmidt coefficients

is called the Schmidt number. Thus, a bipartite pure state is entangled if and only if its Schmidt number is larger than 1.

Schmidt decomposition is an application of singular value decomposition (SVD) in quantum mechanics. The practice and protocol of Schmidt decomposition are the same as SVD.⁷ One needs to trace out one of the subsystems and then diagonalize the reduced density matrix

$$\text{Tr}_A(|\Psi\rangle_{AB}\langle\Psi|_{AB}) = \rho_B = \sum_{n=1}^N \lambda_n |\beta_n\rangle_B \langle\beta_n|_B \quad (31a)$$

$$\text{Tr}_B(|\Psi\rangle_{AB}\langle\Psi|_{AB}) = \rho_A = \sum_{n=1}^N \lambda_n |\alpha_n\rangle_A \langle\alpha_n|_A \quad (31b)$$

The eigenvalues of ρ_B are actually the square of Schmidt coefficients λ_n while the corresponding eigenvectors are the Schmidt bases $|\beta_n\rangle_B$. Use the same protocol to calculate reduced density matrix ρ_A and its eigensvalues λ_n and eigenvectors $|\alpha_n\rangle_A$. It is worth noticing that ρ_A and ρ_B share the same nonzero eigenspectrum λ_n . Many important properties of quantum systems such as expectation values of observables are completely determined by the eigenvalues of the density matrix, so for a bipartite pure state such properties of one subsystem will be identical to those of the other subsystem.⁷

A bipartite pure state $|\Psi\rangle_{AB}$ is separable if and only if its Schmidt number equals 1, so its reduced density matrix ρ_B can only have one nonzero eigenvalue, i.e., ρ_B is pure, which is the separable criterion for bipartite pure states. The purity $\gamma(\rho_B) = \text{Tr}(\rho_B^2) = \sum_{n=1}^N \lambda_n^2$ of the reduced density matrix of a bipartite pure state can describe the separability and entanglement. $\gamma(\rho_B) = 1$ means separability, and $\frac{1}{\min\{N_A, N_B\}} \leq \gamma(\rho_B) < 1$ means entanglement.

A more commonly used quantity for entanglement measurement in quantum information is the entanglement entropy, which is defined as the Von Neumann Entropy of the reduced density matrix

$$E_S(\rho_{AB}) = S(\rho_B) = - \sum_{\lambda_n \neq 0} \lambda_n \ln \lambda_n \quad (32)$$

Entanglement entropy quantifies the entanglement of a bipartite pure state; that is, larger $S(\rho_B)$ indicates a more entangled state. A separable state has zero entanglement entropy $S(\rho_B) = 0$. An entangled state has positive entanglement entropy $S(\rho_B) > 0$. A full entangled state has the maximum entanglement entropy $S(\rho_B) = \ln(\min\{N_A, N_B\})$. Intuitively, the quantities to describe entanglement should not depend on the choice of the subsystem. Actually, $S(\rho_B) = S(\rho_A)$ and $\gamma(\rho_B) = \gamma(\rho_A)$, because entropy and purity are completely determined by the eigenvalues of the reduced density matrix, as stated above.

In the following, we present some examples of the application of Schmidt decomposition and entanglement entropy. Consider a bipartite pure state $|\Psi_1\rangle_{AB} = \frac{1}{2}(|00\rangle + |10\rangle - |01\rangle - |11\rangle)_{AB}$. Using the protocol in eqs 31 and 32, one can calculate $\rho_{1,B} = \frac{1}{2}(|0\rangle\langle 0| + |1\rangle\langle 1| - |0\rangle\langle 1| - |1\rangle\langle 0|)_{BB}$, and $S(\rho_{1,B}) = 0$. Thus, $|\Psi_1\rangle_{AB}$ is a separable state. It can be further verified that $|\Psi_1\rangle_{AB} = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)_A \otimes \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)_B$, which indeed matches eq 26.

A second example is $|\Psi_2\rangle_{AB} = (x|00\rangle + y|11\rangle)_{AB}$, where x and y are the coefficients satisfying $|x|^2 + |y|^2 = 1$. Then, one can work out $\rho_{2,B} = |x|^2|0\rangle_B\langle 0| + (1 - |x|^2)|1\rangle_B\langle 1|$ and thus $S(\rho_{2,B}) = -|x|^2 \ln |x|^2 - (1 - |x|^2) \ln (1 - |x|^2)$. When $x = \frac{1}{2}$, $S(\rho_{2,B}) \approx 0.562$. When $x = \frac{1}{\sqrt{2}}$, $|\Psi_2\rangle_{AB}$ is the Bell state and $S(\rho_{2,B}) = \ln 2 \approx 0.693$. Both states are entangled, but quantitatively the latter contains more entanglement than the former. Actually, all four Bell states (eq 3) are maximally entangled as they have the maximum entanglement entropy $S(\rho_B) = \ln 2$.

Entanglement Measures. In an axiomatic point of view,¹ Vidal et al.⁴⁵ proposed the postulates that any entanglement measure $E(\rho)$ has to satisfy. Here we take bipartite entanglement as an example. Any entanglement measure must satisfy the monotonicity condition:

$$E(\rho_{AB}) \geq E\left(\sum_m M_{A,m} \otimes M_{B,m} \rho_{AB} M_{A,m}^\dagger \otimes M_{B,m}^\dagger\right) \quad (33)$$

where $\{M_{A,m}\}$ and $\{M_{B,m}\}$ are the local POVM of subsystem A and B, respectively. The global POVM $\{M_{A,m} \otimes M_{B,m}\}$ makes $\{M_{A,m}\}$ and $\{M_{B,m}\}$ classically correlated (known as classical communication) and can only increase the classical-like correlation among the subsystems. Equation 33 means that entanglement cannot increase under local operations and classical communication (LOCC), sometimes known as entanglement monotone.⁴⁶ Entanglement monotone is considered the only necessary postulate for an entanglement measure, while other postulates either follow from this basic axiom or should be treated as optional.^{1,47}

However, building general entanglement measures in this framework is difficult and computationally complex, so we are going to focus on the special cases. Apart from the entanglement entropy for bipartite pure states, we show some examples of nonstandard entanglement measures for two-qubit entanglement.

Concurrence. Concurrence was first proposed by Hill and Wootters⁴⁸ based on the fidelity operator $R = \sqrt{\sqrt{\rho_{AB}} \tilde{\rho}_{AB} \sqrt{\rho_{AB}}}$, where $\tilde{\rho}_{AB} = (\sigma_A^x \sigma_B^x) \rho_{AB}^* (\sigma_A^x \sigma_B^x)$ and ρ_{AB}^* is the complex conjugate of ρ_{AB} in σ^z basis. R is Hermitian and has the eigenvalues λ_m in descending order. Concurrence is defined as

$$E_C(\rho_{AB}) = \max\{0, \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4\} \quad (34)$$

Entanglement of Formation. Entanglement of formation⁴⁹ is the ensemble average of entanglement entropy:

$$E_F(\rho_{AB}) = \min_{\{p_i, |\psi_i\rangle_{AB}\}} \left\{ \sum_i p_i E_S(|\psi_i\rangle_{AB}) \right\} \quad (35)$$

where the minimum runs over all the possible decompositions $\rho_{AB} = \sum_i p_i (|\psi_i\rangle\langle\psi_i|)_{AB}$ and $E_S(|\psi_i\rangle_{AB})$ is the entanglement entropy (eq 32). For the two-qubit case, it has the closed-form expression

$$E_F(\rho_{AB}) = H\left(\left\{ \frac{1 + \sqrt{1 - E_C(\rho_{AB})^2}}{2}, \frac{1 - \sqrt{1 - E_C(\rho_{AB})^2}}{2} \right\}\right) \quad (36)$$

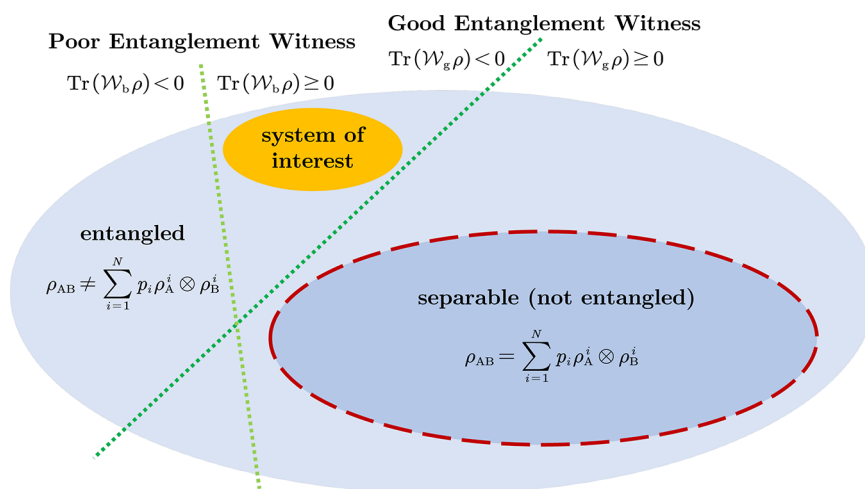


Figure 4. A set of all the bipartite states (Liouville space) as an illustration for entanglement and witness. The red dashed curve is the boundary between entangled states and separable states. The subset of all the separable states is convex. The two green dotted lines represent two examples of hyperplanes that work as entanglement witnesses $\mathcal{W}$. However, only $\mathcal{W}_g$ is a good entanglement witness with respect to the system of interest.

where $E_C(\rho_{AB})$ is the concurrence (eq 34) and $H(\{p_1, p_2\})$ is the Shannon entropy (eq 22) for binomial distribution.

Relative Entropy of Entanglement. Relative entropy of entanglement⁵⁰ is a distance measure between the entangled state ρ_{AB} and the separable set $\mathcal{S}_1$.

$$E_R(\rho_{AB}) = \min_{\rho_{s,AB} \in \mathcal{S}_1} \left\{ \text{Tr} \left(\rho_{AB} \ln \frac{\rho_{AB}}{\rho_{s,AB}} \right) \right\} \quad (37)$$

In the absence of a closed-form expression, Vedral et al.⁴⁵ discussed the properties of $E_R(\rho_{AB})$ for a two-qubit system.

Negativity. Negativity is a computationally feasible entanglement measure,⁵¹ originating from the violation of “positive semidefinite” of the reduced density matrix of an entangled state.

$$E_N(\rho_{AB}) = \frac{\|\rho_B\| - 1}{2} \quad (38)$$

where $\rho_B = \text{Tr}_A(\rho_{AB})$ is the reduced density matrix and $\|\rho_B\| = \text{Tr} \sqrt{\rho_B^\dagger \rho_B}$ is the trace norm.

Entanglement Witness. In general, it is NP-hard to find the sufficient and necessary criterion of entanglement qualitatively.⁴³ Moving a step backward, there are some sufficient but not necessary conditions for entanglement, regardless of the dimension, known as entanglement witnesses.^{52–54} An entanglement witness is a Hermitian operator $\mathcal{W}(\rho)$ that can sufficiently distinguish certain entangled states ρ from all the separable states. Specifically, entanglement witnesses are defined as the Hermitian operators that obey the inequality $\text{Tr}(\mathcal{W}(\rho)\rho) \geq 0$ for all the separable states. Thus, a negative expectation value $\text{Tr}(\mathcal{W}(\rho)\rho) < 0$ means that ρ must be entangled. $\mathcal{W}(\rho)$ may be linear or nonlinear depending on ρ .

The convexity of the set of all separable states ensures the existence of the witness operator $\mathcal{W}(\rho)$ and the validation of an entanglement witness.¹ The Hahn–Banach theorem guarantees that there exists a hyperplane for any entangled state ρ that distinguishes this state from the separable set,⁵² as shown in Figure 4, where the hyperplanes are represented by the green dotted lines. These hyperplanes correspond to

observables $\mathcal{W}(\rho)$, represented by $\text{Tr}(\mathcal{W}(\rho)\rho) = 0$. If there is one separable state that makes $\text{Tr}(\mathcal{W}(\rho)\rho) = 0$, the hyperplane is at a tangent to the convexity set of separable states. Such tangent hyperplanes are usually thought to be efficient entanglement witnesses that reach their tight bound.

It is worth noting that an entanglement witness is just a sufficient but not necessary condition that qualitatively describes entanglement.⁵⁵ $\text{Tr}(\mathcal{W}(\rho)\rho) < 0$ means that ρ must be entangled, while the inverse and the converse may not be true. As shown in Figure 4, some entangled state states satisfy $\text{Tr}(\mathcal{W}(\rho)\rho) \geq 0$. Thus, $\text{Tr}(\mathcal{W}(\rho)\rho) \geq 0$ does not imply that ρ is separable. Entanglement witnesses can only confirm entangled states but cannot exclude that a state is entangled. For the same reason, the expectation value $\text{Tr}(\mathcal{W}(\rho)\rho)$ cannot quantify entanglement; a more negative value of $\text{Tr}(\mathcal{W}(\rho)\rho)$ does not suggest ρ is more entangled.

Bell’s theorem⁵⁶ is a famous example of entanglement witness. There are many different formalisms of Bell’s inequality. Here, we focus on the Clauser–Horne–Shimony–Holt (CHSH) inequality.⁵⁷ Consider a total system ρ_{AB} consisting of two half-spins. If ρ_{AB} is separable, the CHSH inequality holds

$$\begin{aligned} \text{Tr}(\rho \mathcal{W}_{\text{CHSH}}) &= 2 + \langle \sigma_A^{\alpha_2} \sigma_B^{\beta_2} \rangle - \langle \sigma_A^{\alpha_1} \sigma_B^{\beta_1} \rangle - \langle \sigma_A^{\alpha_2} \sigma_B^{\beta_1} \rangle \\ &\quad - \langle \sigma_A^{\alpha_1} \sigma_B^{\beta_2} \rangle \geq 0 \end{aligned} \quad (39)$$

where $\sigma^\alpha = \vec{\alpha} \cdot \vec{\sigma}$ and $\langle \sigma_A^{\alpha_2} \sigma_B^{\beta_2} \rangle = \text{Tr}(\rho_{AB} \sigma_A^{\alpha_2} \sigma_B^{\beta_2})$. Although separable states always satisfy the CHSH inequality, entangled states may disobey Bell’s theorem. In this sense, the CHSH inequality (and other Bell’s inequalities) can work as entanglement witnesses, because a quantum state not satisfying eq 39 must be entangled. We can test the CHSH inequality by taking the unit vectors $\alpha_1 = (0, 0, 1)$, $\alpha_2 = (1, 0, 0)$, $\beta_1 = (-\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}})$, $\beta_2 = (\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}})$, and the singlet state $|\psi\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)_{AB}$. We then work out $\langle \psi | \mathcal{W}_{\text{CHSH}} | \psi \rangle = 2(1 - \sqrt{2}) < 0$, which proves that the singlet state is entangled. This agrees with the entanglement entropy for the Bell state.

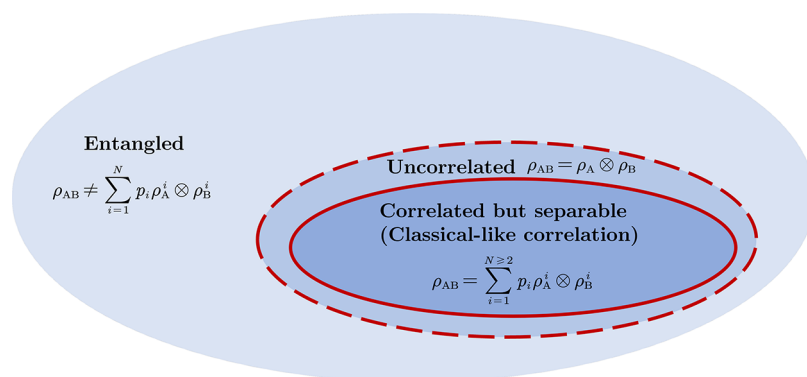


Figure 5. A set of all the bipartite states (Liouville space) as an illustration for entanglement and correlation. The red solid curve is the boundary between correlated states and uncorrelated states. The red dashed curve is the boundary between entangled states and separable states. The ellipses imply convexity. Notice that all the uncorrelated states comprise the convex hull of the separable set. Thus, the uncorrelated set is the edge of the separable ellipse.

The choice of entanglement witness operator $\text{Tr}(\mathcal{W}(\rho)\rho)$ is not unique, because there are infinite witness hyperplanes in the Liouville space. For example, there is an arbitrariness in choosing the direction of the unit vector $\vec{\alpha}$ and $\vec{\beta}$ in eq 39. Apart from Bell's theorem, variance and quantum Fisher information are also relevant to building entanglement witnesses. Among so many entanglement witnesses, their performance varies based on the system of interest. Specifically, entanglement witnesses with negative expectation values regarding the system of interest are good entanglement witnesses. Figure 4 shows two examples, $\mathcal{W}_g$ and $\mathcal{W}_b$, where $\mathcal{W}_g$ is a good entanglement witness for the system of interest but $\mathcal{W}_b$ is not a suitable witness for the underlying state.

The example of the CHSH inequality also shows that some witnesses are not good when studying the singlet state. If we take $\alpha_1 = (0, 0, 1)$, $\alpha_2 = (1, 0, 0)$, $\beta_1 = \beta_2 = (0, 0, 1)$ in eq 39, the singlet state $|\psi\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)_{AB}$ gives the expectation value of $\langle\psi|\mathcal{W}_{\text{CHSH}}|\psi\rangle = 2 - \sqrt{2} \geq 0$. The challenge hence lies in the construction of useful entanglement witnesses, tailored for the systems and properties of interest produced in an experiment. In the Bell test, the correlation between different spin projections is measured to get a powerful entanglement witness.

Entanglement witnesses also offer a feasible way to advise experimentalists on how to prove the existence of entanglement in a quantum system, because we only need to detect the expectation value of a suitable observable. Entanglement witnesses are usually treated as one of the most important practical entanglement certification techniques.⁵² For example, Aspect's experiment is a Bell test that proves the violation of Bell inequalities by measuring the correlation between entangled photons.⁵⁸ It has recently been shown that quantum Fisher information on certain states of a molecular aggregate or polariton system can be measured by linear absorption spectroscopy,⁵⁹ and an entanglement witness operator $\mathcal{W}_{\text{QFI}}(\rho)$ can be built by quantum Fisher information.

Take polariton chemistry as an example. It has been shown that in the typical electronic coupling regime, $\mathcal{W}_{\text{QFI}}(\rho)$ works as a good multimolecular entanglement witness at room temperature and can be measured by bound mode absorption. This is rigorous proof of the existence of long-lived multimolecular entanglement because of intramolecular interaction indirectly induced by cavity QED, despite the

dephasing due to the system–bath interaction at room temperature.⁶⁰

Correlation and Coherence. In classical statistics, covariance $\text{cov}[X, Y]$ describes the correlation between two random variables X and Y : $\text{cov}[X, Y] = E[XY] - E[X]E[Y]$, where $E[X]$, $E[Y]$, and $E[XY]$ are the expectation values of the X , Y , and their product XY . In quantum mechanics, to study the correlation between two quantities or operators, the correlation function can be similarly written as $\text{Tr}(\rho O_1 O_2) - \text{Tr}(\rho O_1)\text{Tr}(\rho O_2)$. It is convenient to assume O_1 and O_2 have zero expectation value. Otherwise, we may redefine the operators by shifting the operators with a constant as $O' = O - \text{Tr}(\rho O)$. Typically, the two-point correlation function is defined as

$$\langle O_1 O_2 \rangle = \text{Tr}(\rho O_1 O_2) \quad (40)$$

where the operators do not have to be observable.

The quantification of correlation is well-defined and has been widely studied in physics and chemistry. For example, in molecular spectroscopy, it is predicted using autocorrelation of the dipole operator^{61,62} as $\langle\mu(t)\mu(0)\rangle$. In many-body physics and field theory, the two-point correlator between creation and annihilation operators in the time-order $\langle T a_k(t) a_k^\dagger(t') \rangle$ is the time-ordered Green's function and propagator.⁶³ In quantum optics, correlation functions are used to characterize the statistical and coherence properties of an electromagnetic field $\mathcal{E}(\vec{r}, t)$, known as the degree of coherence⁶⁴

$g^{(1)} = \frac{\langle \mathcal{E}^*(\vec{r}_1, t_1) \mathcal{E}(\vec{r}_2, t_2) \rangle}{\sqrt{\langle |\mathcal{E}(\vec{r}_1, t_1)|^2 \rangle \langle |\mathcal{E}(\vec{r}_2, t_2)|^2 \rangle}}$, where the phase is encoded in the

complex field $\mathcal{E}$. Similarly, the n -point correlation function can be generalized, for example, to study the higher-order Dyson series in nonlinear spectroscopy or the degree of second-order coherence⁶⁴ $g^{(2)} = \frac{\langle \mathcal{E}^*(\vec{r}_1, t_1) \mathcal{E}^*(\vec{r}_2, t_2) \mathcal{E}(\vec{r}_1, t_1) \mathcal{E}(\vec{r}_2, t_2) \rangle}{\langle |\mathcal{E}(\vec{r}_1, t_1)|^2 \rangle \langle |\mathcal{E}(\vec{r}_2, t_2)|^2 \rangle}$.

In this paper, we are more interested in the correlation between two subsystems, to clarify the difference between quantum correlation and classical correlation, and their relation to the entanglement between two subsystems. In this case, we take O_A and O_B as two local operators on two subsystems in eq 40. The concept of quantum coherence is also clarified because when calculating the correlation function, there will be a contribution from coherence.

Quantum Correlation. Two subsystems that are entangled with each other imply a quantum correlation between them. Quantum entanglement is a special form of quantum

correlation without classical analogy. To further clarify this statement, we first define the uncorrelated quantum state, which is composed of an uncorrelated pair of subsystems:

$$\rho_{AB} = \rho_A \otimes \rho_B \quad (41)$$

To find such tensor product decomposition, partial trace can be applied: $\rho_A = \text{Tr}_B(\rho_{AB})$ and $\rho_B = \text{Tr}_A(\rho_{AB})$. If one carries out a local measurement on subsystem A by a local operator O_A , the expectation value $\langle O_A \rangle = \text{Tr}(O_A \rho_{AB}) = \text{Tr}(O_A \rho_A)$ is completely determined by the information about subsystem A and no information will be gained for B from this measurement. No mutual information is lost during the measurement. Similarly, the two-point correlator of an uncorrelated pair is $\langle O_A O_B \rangle = \langle O_A \rangle \langle O_B \rangle$, which is simply the multiplication of two expectation values with no cross-term. Thus, we can reconstruct the uncorrelated quantum state ρ_{AB} by doing quantum tomography independently on subsystems A and B. Equation 41 defines the uncorrelated quantum states. A classical analogy to uncorrelated quantum systems is independence in classical probability theory, where the joint probability of a pair of random variables (X, Y) can be written as the product of their probabilities: $P_{XY}(x, y) = P_X(x)P_Y(y)$.

A state with quantum correlation between two subsystems is then defined as a quantum state that is not uncorrelated, which means that the density matrix cannot be written as a tensor product of the reduced density matrices:

$$\rho_{AB} \neq \text{Tr}_B(\rho_{AB}) \otimes \text{Tr}_A(\rho_{AB}) = \rho_A \otimes \rho_B \quad (42)$$

The distinction between correlated and uncorrelated systems is demonstrated in Figure 5 by the red solid curve. Equation 42 offers a simple criterion to examine if a system is correlated. Furthermore, quantum correlation can sometimes be quantified by the distance between ρ_{AB} and $\rho_A \otimes \rho_B$, for example, fidelity $F(\rho_{AB}, \rho_A \otimes \rho_B) = (\text{Tr}(\sqrt{\sqrt{\rho_{AB}}(\rho_A \otimes \rho_B)\sqrt{\rho_{AB}}}))^2$, trace distance $T(\rho_{AB}, \rho_A \otimes \rho_B) = \frac{1}{2}\text{Tr}(\sqrt{(\rho_{AB} - \rho_A \otimes \rho_B)^2})$, and relative entropy (also known as quantum mutual information in this case) $I(\rho_{AB}, \rho_A \otimes \rho_B) = \text{Tr}\left(\rho_{AB} \ln\left(\frac{\rho_{AB}}{\rho_A \otimes \rho_B}\right)\right) = S(\rho_A) + S(\rho_B) - S(\rho_{AB})$.

As stated before, quantum entanglement is a special form of quantum correlation. Similarly, by comparing separable states (eq 27) and uncorrelated states (eq 41), one can find that the uncorrelated state is a special form of the separable state. Uncorrelated states comprise the convex hull of the separate set. Therefore, there exists a set of density matrices that is correlated but separable (not entangled), known as classical-like correlation:

$$\rho_{AB} = \sum_{i=1}^{n \geq 2} p_i \rho_A^i \otimes \rho_B^i \quad (43)$$

where $p_i > 0$ and $\sum_i p_i = 1$ with at least 2 nonzero terms. The classical analogy in probability theory is $P_{XY}(x, y) = \sum_{i=1}^{n \geq 2} p_i P_X^i(x) P_Y^i(y)$. Here is an example of a correlated but not entangled state:

$$\rho_{AB}^{(1)} = \frac{1}{2}(|00\rangle\langle 00| + |11\rangle\langle 11|)_{AB} \quad (44)$$

If we do a one-time measurement on subsystem A by the local operator σ_A^z and get $|0\rangle_A$, we can predict that the following measurement by the local operator σ_B^z will result in $|0\rangle_B$, and

vice versa. Therefore, $\rho_{AB}^{(1)}$ shows a strong correlation between subsystems A and B, despite it being separable. This correlation is classical-like.

On the contrary, a Bell state $|\Phi_+\rangle_{AB} = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)_{AB}$, or $\rho_{AB}^{(2)} = |\Phi_+\rangle_{AB}\langle\Phi_+|_{AB}$, is entangled. However, $\rho_{AB}^{(2)}$ contains some similar intersystem correlation to $\rho_{AB}^{(1)}$, because if we do a local projective measurement σ_A^z first, followed by σ_B^z , we will get the same results as for $\rho_{AB}^{(1)}$. Thus, entangled states and classical-like correlated states share the same local measurement outcome and the same correlation function, $\langle \sigma_A^z \sigma_B^z \rangle^{(1)} = \langle \sigma_A^z \sigma_B^z \rangle^{(2)} = 1$, which means correlation is not solid evidence of entanglement.

To better understand this, we write the Bell state as a density matrix $\rho_{AB}^{(2)} = |\Phi_+\rangle_{AB}\langle\Phi_+|_{AB}$ and expand it:

$$\rho_{AB}^{(2)} = \frac{1}{2}(|00\rangle\langle 00| + |11\rangle\langle 11| + |00\rangle\langle 11| + |11\rangle\langle 00|)_{AB} \quad (45)$$

It is now clear that $\rho_{AB}^{(2)}$ has nonzero quantum coherence in the chosen basis, while $\rho_{AB}^{(1)}$ does not. So, it is the quantum coherence that induces the nonclassical entanglement. When performing local projective measurements on one subsystem, we only keep the reduced density and lose coherence, which is actually a dephasing process. $\rho_{AB}^{(2)}$ will dephase to $\rho_{AB}^{(1)}$ when it strongly interacts with the measurement instrument. We can further check that $\rho_{AB}^{(1)}$ and $\rho_{AB}^{(2)}$ share the same reduced density matrix:

$$\text{Tr}_B(\rho_{AB}^{(1)}) = \text{Tr}_B(\rho_{AB}^{(2)}) = \frac{1}{2}(|0\rangle\langle 0| + |1\rangle\langle 1|)_A \quad (46)$$

Although quantum correlation is a more general concept than quantum entanglement, they are related. Correlation functions can be used as entanglement witnesses that sufficiently distinguish some entangled states, and the correlation functions are easy to measure and quantify. As an example discussed before, Bell's inequality (eq 39) offers some constraint of the two-point correlation functions for the separable states, including those classical-like correlated states, but the entangled states are not bounded by it. In the Bell test, the quantum correlation is revealed by noting that the singlet spin state is unchanged by observing it in any reference frame (e.g., the observer can rotate the axes and still measure the same spin-pairing). Bell realized that the extra quantum correlation can often (but not always) be detected by comparing two measurements performed in different reference frames.⁸

Quantum Coherence. The previous example shows that the entangled state is not only correlated but also violates locality and realism. The distinction between classical-like correlation and quantum entanglement can be understood by quantum coherence. The concept of coherence originates from wave interference, where the phase difference leads to constructive or destructive interference. In quantum mechanics, a pure state is just a wave function. As shown in eq 2, $|\langle 10|0\rangle|$ shows the effect of interference and $c_0 c_1^*$ quantifies the magnitude of interference, known as quantum coherence.

More rigorously, the concept of quantum coherence needs to be discussed in the density matrix formalism. Quantum coherence is signaled by the off-diagonal terms of a density matrix in a particular basis. When studying a density matrix in this fixed basis, the diagonal terms are considered a series of classical-like probabilities, while the off-diagonal terms emphasize the quantum properties of the state. Thus, a

diagonal density matrix is considered classical-like in this fixed basis. When doing PVM, we project the quantum state ρ to this fixed basis by keeping only the diagonal terms and dropping all the coherence, resulting in an incoherent and classical-like quantum state $\rho' = \sum_i P_m \rho P_m$.

It is important to point out that coherence varies in different bases of the same quantum state. So specifying the basis is the first step to studying coherence.

To quantify quantum coherence in a fixed basis, we follow the rule of monotonicity under incoherent operations (quantum operations that map the set of incoherent states onto itself). Baumgratz et al.⁶⁵ proposed the l_1 -norm coherence

$$C_{l_1}(\rho) = \sum_{m_1, m_2} |\langle m_1 | (\rho - \rho') | m_2 \rangle| = \sum_{m_1 \neq m_2} |\rho_{m_1, m_2}| \quad (47)$$

which is the sum of all the l_1 -norm of the off-diagonal terms. The relative entropy coherence is defined as

$$C_{r.e.}(\rho) = \text{Tr} \left(\rho \ln \left(\frac{\rho}{\rho'} \right) \right) = S(\rho') - S(\rho) \quad (48)$$

which is just the difference between the von Neumann entropy of ρ' and ρ , where the positivity is guaranteed by eq 25.

Although relevant, quantum coherence is very different from quantum correlation and quantum entanglement. Either quantum correlation (uncorrelatedness) or quantum entanglement (separability) is basis-independent, unlike quantum coherence. Intuitively, the correlation or entanglement between the two subsystems should not depend on the basis chosen to describe the composite system.

CONCLUSION

In this article, we reviewed some basic concepts in quantum information by providing rigorous mathematical definitions and physical pictures. We attempted to frame the paper especially for researchers in chemistry and other fields outside of quantum physics. In particular, we emphasized the basic tools needed to deal with the generalization of classical probability theory in classic information theory to density matrix theory, which is central to quantum information.

With the definition of mixed states, quantum measurements, and the von Neumann entropy, entanglement can be rigorously discussed. Although chemistry is dominated by quantum mechanics, many chemical systems are classical-like and can be well-described in the classical context. Entanglement is of great interest because it has no classical analogy, which implies that it can be exploited in ways not possible for classical systems. Entanglement is defined as a state that cannot be written as a convex combination of the tensor product states of the subsystems. For a bipartite pure state, entanglement entropy (eq 32) quantifies entanglement. While small model systems can be well studied, chemistry will likely shift focus to much larger quantum systems. A key point to realize is that it is NP-hard to pinpoint a general state (with an arbitrary number of particles and arbitrary dimension) as being entangled⁴³ and thus difficult to measure entanglement.⁴⁵ A sufficient approach to qualitatively describe multipartite entanglement involves entanglement witnesses, such as Bell's inequality,⁵⁸ variance,⁵² or quantum Fisher information.^{59,60} These kinds of techniques and developments thereof will be of interest for classifying chemical entanglement.

It is sometimes easy to get confused between quantum entanglement, quantum correlation, and quantum coherence,

which, though related, are fundamentally different. Quantum entanglement is a special form of quantum correlation, but correlation does not always mean entanglement. The disentangled correlation is known as the classical-like correlation. Quantum correlation can be easily quantified by correlation function both theoretically and experimentally, but it is usually an NP-hard problem to describe entanglement. Quantum entanglement is the quantum correlation with no classical analogy, where the nontrivial quantum effect is guaranteed by quantum coherence in a fixed basis. However, quantum coherence does not mean quantum entanglement, because entanglement and correlation are basis-independent, but coherence varies with the choice of basis.

Quantum correlation can be used to build entanglement witnesses. For example, the Bell test aims to measure the correlation between spins in different directions to sufficiently detect entanglement. Linear absorption spectroscopy can measure the dipole autocorrelator to witness entanglement. As anticipated above, quantum entanglement defies explanation by classical-like correlation. Moreover, we showed how certain types of quantum correlations come hand-in-hand with their possible classical analogies, and often the classical correlations dominate, for example, the adiabatic dynamics and Markovian dynamics. Physically, this is the same idea that is exemplified by interference, as seen in the double-slit experiment. Interference is insufficient evidence for distinctly quantum correlations, even though it evidences wave-like properties.

There are many examples of classical correlations exhibited by chemical systems. These include synchronization produced by feedback loops, oscillating reactions, or any switched system under kinetic control. Although these are interesting phenomena, they are not directly relevant to the nontrivial features of quantum information. To build the nontrivial features of entanglement between molecules, intermolecular interaction is required, and entanglement grows at a rate proportional to the interaction.⁶⁶ However, in chemistry, due to the noisy environment (i.e., the system–bath interaction), large dephasing destroys entanglement, rendering the system classical-like. Such chemical systems show mostly classical behavior and lack the long-lived quantum entanglement needed in quantum information applications. So we need to understand entanglement to engineer chemical systems for quantum information. To build entanglement and maintain it for a longer time, one way forward is using larger intermolecular interactions that can compete with dephasing, such as molecular aggregates⁶⁷ or cavity QED.^{68–70} Entanglement witnesses such as quantum Fisher information⁶⁰ could be useful to sufficiently prove the existence of entanglement.

We hope this detailed Mini-Review serves as a helpful primer to provide rigorous background on quantum information. That, in turn, will serve as a platform for discovering new examples of, and tools to study, quantum information in the molecular domain.

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Notes

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REFERENCES

- (1) Horodecki, R.; Horodecki, P.; Horodecki, M.; Horodecki, K. Quantum entanglement. *Reviews of modern physics* **2009**, *81*, 865.
- (2) Saffman, M.; Walker, T. G.; Mølmer, K. Quantum information with Rydberg atoms. *Reviews of modern physics* **2010**, *82*, 2313.
- (3) Kaufman, A. M.; Ni, K.-K. Quantum science with optical tweezer arrays of ultracold atoms and molecules. *Nat. Phys.* **2021**, *17*, 1324–1333.
- (4) Chitambar, E.; Gour, G. Quantum resource theories. *Reviews of modern physics* **2019**, *91*, No. 025001.
- (5) Scholes, G. D. A molecular perspective on quantum information. *Proceedings of the Royal Society A* **2023**, *479*, 20230599.
- (6) Wasielewski, M. R.; et al. Exploiting chemistry and molecular systems for quantum information science. *Nature Rev. Chem.* **2020**, *4*, 490–504.
- (7) Nielsen, M. A.; Chuang, I. L. *Quantum Computation and Quantum Information*; Cambridge University Press: Cambridge, 2016.
- (8) Ballentine, L. E. *Quantum Mechanics: A modern development*; World Scientific: Singapore, 2015.
- (9) Peres, A. *Quantum Theory: Concepts and Methods*; Kluwer: Dordrecht, 1995.
- (10) Barnett, S. M. *Quantum Information*; Oxford University Press: Oxford, 2009.
- (11) Kais, S. Introduction to quantum information and computation for chemistry. *Quantum Information and Computation for Chemistry* **2014**, 1–38.
- (12) Jeong, H.; Kim, M.; Lee, J. Quantum-information processing for a coherent superposition state via a mixed-entangled coherent channel. *Phys. Rev. A* **2001**, *64*, No. 052308.
- (13) Kais, S. Entanglement, electron correlation, and density matrices. *Advances in Chemical Physics* **2007**, *134*, 493.
- (14) Kadison, R. V.; Ringrose, J. R. *Fundamentals of the theory of operator algebras*; American Mathematical Society: Providence RI, 1997.
- (15) Webster, R. *Convexity*; Oxford University Press: Oxford, 1994.
- (16) Kramer, B.; MacKinnon, A. Localization: theory and experiment. *Rep. Prog. Phys.* **1993**, *56*, 1469.
- (17) Evers, F.; Mirlin, A. Fluctuations of the inverse participation ratio at the Anderson transition. *Physical review letters* **2000**, *84*, 3690.
- (18) Wegner, F. Inverse participation ratio in $2 + \epsilon$ dimensions. *Zeitschrift für Physik B Condensed Matter* **1980**, *36*, 209–214.
- (19) Ma, J.; Wang, X.; Sun, C.-P.; Nori, F. Quantum spin squeezing. *Phys. Rep.* **2011**, *509*, 89–165.
- (20) Kitagawa, M.; Ueda, M. Squeezed spin states. *Phys. Rev. A* **1993**, *47*, 5138.
- (21) Einstein, A.; Podolsky, B.; Rosen, N. Can Quantum-Mechanical Description of Physical Reality be Considered Complete? *Phys. Rev.* **1935**, *47*, 777–780.
- (22) Holevo, A. *Probabilistic and Statistical Aspects of Quantum Theory*; Edizioni della Normale: Pisa, 2011.
- (23) Lenglé, B.; Stone, M. Elementary proof of the spectral theorem. *Annals of Mathematics* **1936**, *37*, 853–864.
- (24) Tong, D.; Chen, J.-L.; Huang, J.; Kwek, L.; Oh, C. Kraus representation for the density operator of a qubit. *Laser physics* **2006**, *16*, 1512–1516.
- (25) Kraus, K. *States, Effects, and Operations: Fundamental Notions of Quantum Theory*; Lecture Notes in Physics; Springer: Berlin, 1983; Vol. 190.
- (26) Busch, P.; Lahti, P.; Pellonpää, J.-P.; Ylinen, K.; *Quantum Measurement*; Springer: Switzerland, 2016.
- (27) Davies, E. B.; Lewis, J. T. An operational approach to quantum probability. *Communications in Mathematical Physics* **1970**, *17*, 239–260.
- (28) Ozawa, M. Quantum Measuring Processes of Continuous Observables. *J. Math. Phys.* **1984**, *25*, 79–87.
- (29) Jacobs, K.; Steck, D. A. A straightforward introduction to continuous quantum measurement. *Contemp. Phys.* **2006**, *47*, 279–303.
- (30) Stone, J. V. *Information Theory: A tutorial introduction*; Seibel Press: Middletown, DE, 2015.
- (31) Ash, R. B. *Information Theory*; Dover: New York, 1990.
- (32) Shannon, C. E. A mathematical theory of communication. *Bell system technical journal* **1948**, *27*, 379–423.
- (33) Yuen, H.; Ozawa, M. Ultimate Information Carrying Limit of Quantum-Systems. *Phys. Rev. Lett.* **1993**, *70*, 363–366.
- (34) Mattle, K.; Weinfurter, H.; Kwiat, P.; Zeilinger, A. Dense coding in experimental quantum communication. *Phys. Rev. Lett.* **1996**, *76*, 4656–4659.
- (35) Gisin, N.; Thew, R. Quantum communication. *Nat. Photonics* **2007**, *1*, 165–171.
- (36) Bennett, C. H.; Brassard, G. Quantum cryptography: Public key distribution and coin tossing. *Theor. Comp. Science* **2014**, *560*, 7–11.
- (37) Pirandola, S.; et al. Advances in quantum cryptography. *Adv. Opt. Photonics* **2020**, *12*, 1012–1236.
- (38) Werner, R. F. Quantum states with Einstein-Podolsky-Rosen correlations admitting a hidden-variable model. *Phys. Rev. A* **1989**, *40*, 4277.
- (39) Wu, W.; Sifain, A. E.; Delo, C. A.; Scholes, G. D. Polariton enhanced free charge carrier generation in donor–acceptor cavity systems by a second-hybridization mechanism. *J. Chem. Phys.* **2022**, *157*, 161102 DOI: [10.1063/5.0122497](https://doi.org/10.1063/5.0122497).
- (40) Breuer, H.-P.; Laine, E.-M.; Piilo, J.; Vacchini, B. Colloquium: Non-Markovian dynamics in open quantum systems. *Rev. Mod. Phys.* **2016**, *88*, No. 021002.
- (41) Izmaylov, A. F.; Franco, I. Entanglement in the Born–Oppenheimer approximation. *J. Chem. Theory Comput.* **2017**, *13*, 20–28.
- (42) Tully, J. C. Perspective: Nonadiabatic dynamics theory. *J. Chem. Phys.* **2012**, *137*, 22A301.
- (43) Gurvits, L. Classical complexity and quantum entanglement. *Journal of Computer and System Sciences* **2004**, *69*, 448–484.
- (44) Acín, A.; Andrianov, A.; Costa, L.; Jané, E.; Latorre, J.; Tarrach, R. Generalized Schmidt decomposition and classification of three-qubit states. *Phys. Rev. Lett.* **2000**, *85*, 1560.
- (45) Vedral, V.; Plenio, M.; Rippin, M.; Knight, P. Quantifying entanglement. *Phys. Rev. Lett.* **1997**, *78*, 2275–2279.
- (46) Vidal, G. Entanglement monotones. *Journal of Modern Optics* **2000**, *47*, 355–376.
- (47) Popescu, S.; Rohrlich, D. Thermodynamics and the measure of entanglement. *Phys. Rev. A* **1997**, *56*, R3319.
- (48) Hill, S. A.; Wootters, W. K. Entanglement of a pair of quantum bits. *Physical review letters* **1997**, *78*, 5022.
- (49) Wootters, W. K. Entanglement of formation of an arbitrary state of two qubits. *Phys. Rev. Lett.* **1998**, *80*, 2245.
- (50) Vedral, V. The role of relative entropy in quantum information theory. *Rev. Mod. Phys.* **2002**, *74*, 197–234.
- (51) Vidal, G.; Werner, R. F. Computable measure of entanglement. *Phys. Rev. A* **2002**, *65*, No. 032314.
- (52) Friis, N.; Vitagliano, G.; Malik, M.; Huber, M. Entanglement certification from theory to experiment. *Nature Reviews Physics* **2019**, *1*, 72–87.

- (53) Gühne, O.; Tóth, G. Entanglement detection. *Phys. Rep.* **2009**, *474*, 1–75.
- (54) Terhal, B. M. Bell inequalities and the separability criterion. *Phys. Lett. A* **2000**, *271*, 319–326.
- (55) Peres, A. Separability criterion for density matrices. *Phys. Rev. Lett.* **1996**, *77*, 1413–1415.
- (56) Bell, J. S. On the einstein podolsky rosen paradox. *Physique Physique Fizika* **1964**, *1*, 195.
- (57) Collins, D.; Gisin, N. A relevant two qubit Bell inequality inequivalent to the CHSH inequality. *Journal of Physics A: Mathematical and General* **2004**, *37*, 1775.
- (58) Aspect, A. Proposed experiment to test the nonseparability of quantum mechanics. *Physical review D* **1976**, *14*, 1944.
- (59) Sifain, A. E.; Fassioli, F.; Scholes, G. D. Toward witnessing molecular exciton entanglement from spectroscopy. *Phys. Rev. A* **2021**, *104*, No. 042416.
- (60) Wu, W.; Fassioli, F.; Huse, D. A.; Scholes, G. D. Molecular Entanglement Witness by Absorption Spectroscopy in Polariton Chemistry. To be submitted.
- (61) Bloembergen, N. Nonlinear optics and spectroscopy. *Rev. Mod. Phys.* **1982**, *54*, 685.
- (62) Shen, Y.-R. *Principles of nonlinear optics*. 1984.
- (63) Peskin, M. E. *An introduction to quantum field theory*; CRC Press, 2018.
- (64) Zernike, F. The concept of degree of coherence and its application to optical problems. *Physica* **1938**, *5*, 785–795.
- (65) Baumgratz, T.; Cramer, M.; Plenio, M. B. Quantifying coherence. *Physical review letters* **2014**, *113*, 140401.
- (66) Li, Z.-Z.; Chen, W.; Abbasi, M.; Murch, K. W.; Whaley, K. B. Speeding up entanglement generation by proximity to higher-order exceptional points. *Phys. Rev. Lett.* **2023**, *131*, 100202.
- (67) Hestand, N. J.; Spano, F. C. Expanded theory of H-and J-molecular aggregates: the effects of vibronic coupling and intermolecular charge transfer. *Chem. Rev.* **2018**, *118*, 7069–7163.
- (68) Frisk Kockum, A.; Miranowicz, A.; De Liberato, S.; Savasta, S.; Nori, F. Ultrastrong coupling between light and matter. *Nature Reviews Physics* **2019**, *1*, 19–40.
- (69) Forn-Díaz, P.; Lamata, L.; Rico, E.; Kono, J.; Solano, E. Ultrastrong coupling regimes of light-matter interaction. *Rev. Mod. Phys.* **2019**, *91*, No. 025005.
- (70) Mandal, A.; Taylor, M. A.; Weight, B. M.; Koessler, E. R.; Li, X.; Huo, P. Theoretical advances in polariton chemistry and molecular cavity quantum electrodynamics. *Chem. Rev.* **2023**, *123*, 9786–9879.