Entanglement classifier in chemical reactions

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The Einstein, Podolsky, and Rosen (EPR) entanglement, which features the essential difference between classical and quantum physics, has received wide theoretical and experimental attentions. Recently, the desire to understand and create quantum entanglement between particles such as spins, photons, atoms, and molecules is fueled by the development of quantum teleportation, quantum communication, quantum cryptography, and quantum computation. Although most of the work has focused on showing that entanglement violates the famous Bell’s inequality and its generalization for discrete measurements, few recent attempts focus on continuous measurement results. Here, we have developed a general practical inequality to test entanglement for continuous measurement results, particularly scattering of chemical reactions. After we explain how to implement this inequality to classify entanglement in scattering experiments, we propose a specific chemical reaction to test the violation of this inequality. The method is general and could be used to classify entanglement for continuous measurement results.

INTRODUCTION

Entanglement, which is a quantum mechanical property that describes a correlation between quantum mechanical systems that has no classical analog, was introduced by Schrödinger in 1935 (1). This phenomenon was the subject of the famous paper by Einstein, Podolsky, and Rosen, known as the EPR paradox (2), where they considered such behavior to be impossible and argued that the accepted formulation of quantum mechanics must therefore be incomplete. The debate lasted for nearly 30 years until the proposal of Bell’s inequality, which is violated by entanglement (3). Entanglement effect was verified experimentally (4) in tests where the polarization of photons and spins of entangled particles were measured to be statistically violating Bell’s inequality. Nowadays entanglement has become an extremely important physical resource for many applications in quantum communication (5–8) and quantum computation (9–15).

Two-particle entanglement has long been demonstrated experimentally, and recently, there are notable achievements to generate entanglement between three and more spatially separated particle systems. For instance, a 10-photon entanglement system was successfully generated experimentally in 2016 (16, 17). There are also observations of entanglement in quantum dots (18), nitrogen-vacancy center (NV) in diamond (19), trapped ions (20), and even entanglement between photon and quantum dots (21).

It is very important in all of these experiments to be able to quantify or measure the entanglement. Several methods have been proposed to address this question such as entanglement witnesses (22), entropic inequalities (23), and quantum state classifier based on machine learning (24). However, most of these methods are designed for discrete measurement results. Although there are a few successful theoretical analyses for continuous measurement results, they have focused mainly on photonic systems (25–27). The most widely used method to classify entanglement is quantum tomography, by which one could obtain the density matrix of the system (28) from experimental measurements. However, quantum tomography is more time- and resource-consuming as it scales exponentially with the system size (29).

Here, we propose a general practical method to classify entanglement for continuous measurement results. We introduce auxiliary functions to simplify the complicated measurement results and develop a generalized Bell-type inequality for continuous measurements. We also propose an experimental design to test the method in scattering of chemical reactions. Here, we designed a practicable experiment based on the recent scattering experiments of the oriented hydrogen deuteride (HD) and H₂ molecules (30). On the basis of the recent experimental data of Zare and co-workers (30), we simulate the possible measurement results and demonstrate how to distinguish entangled states from unentangled ones. Moreover, our work also provides the possibility to classify entanglement in other chemical reactions as suggested by Brumer and co-workers for entanglement-assisted coherent control in chemical reactions (31, 32).

BELL’S INEQUALITY FOR CONTINUOUS MEASUREMENT RESULTS

We start by preparing N-particles in a pure state |Φ⟩. If we perform an r-th measurement on them, then they will collapse on the eigenstate set { |ϕᵢ⟩₀, |ϕᵢ⟩₁, ⋯, |ϕᵢ⟩ₙ } . Then, we could expand |Φ⟩ as

\[ \left| \Phi \right\rangle = \sum_{i=0}^{n} \alpha_i \left| \phi_i \right\rangle \]

where |ϕᵢ⟩₀ is the i-th eigenstate corresponding to the measurement r, and |Φ⟩ is normalized, \( \sum_{i=0}^{n} |\alpha_i|^2 = 1 \). Performing measurement r, we can obtain the measurement results (denoted here by spectrum) S( |Φ⟩⟨Φ| , r , x), where ( |Φ⟩⟨Φ| is the density matrix, r represents the measurement r, and the variable x could be, for instance, the scattering angle in the scattering experiment.

The distribution of the measurement results (spectrum) can be written as

\[ S( |\phi_i⟩_r \langle \phi_i| , r , x) = \sum_{i=0}^{n} |\alpha_i|^2 \cdot S( |\phi_i⟩_0 \langle \phi_i| , r , x) \]

where S( |ϕᵢ⟩₀ ⟨ϕᵢ| , r , x) is the spectrum of the state |ϕᵢ⟩₀ under the r-th measurement.

In the case of the spin system to be discussed in the Supplementary Materials, a quite common example satisfying Eq. 2 is the measurement in the Stern-Gerlach (SG) experiment (33) of spin \( \frac{1}{2} \) particles. If the particles are prepared in the pure state, then

\[ |\Phi⟩ = \alpha^+_z \left| \uparrow \right⟩ + \alpha^-_z \left| \downarrow \right⟩ \]
Then, providing enough particles to go through that apparatus, the final spectrum can be written as

\[ S(\Phi, \Phi, r, x) = |\alpha_r^+|^2 \cdot S(|\uparrow\rangle \langle \uparrow|, z, x) + |\alpha_r^-|^2 \cdot S(|\downarrow\rangle \langle \downarrow|, z, x) \]

Here, \( z \) represents the direction of the magnetic field in the SG apparatus, and \( S(|\uparrow\rangle \langle \uparrow|, z, x) \) and \( S(|\downarrow\rangle \langle \downarrow|, z, x) \) describe the distribution of particles detected at different locations, \( x \), on the screen for particles at states \( |\uparrow\rangle \) and \( |\downarrow\rangle \), respectively.

If these particles are prepared as a mixed state whose density matrix is expanded in the basis set \( \{|\phi_k^+ \phi_k^-angle\} \),

\[ \rho = \sum_{j=1}^m p_j |\Psi_j\rangle \langle \Psi_j| \]

where \( \sum_{j=1}^m p_j = 1 \). The spectrum under the \( r \)-th measurement is given by

\[ S(\rho, r, x) = \sum_{j=1}^m p_j S(\Phi_j, \Phi_j, r, x) \]  

In the following section, we will assume that Eqs. 2 and 4 are always satisfied, and we will mainly focus on two-particle systems. Generally, if we use \( |\Psi\rangle \) to represent a pure state of the two-particle system, then its density matrix can be written as

\[ \rho = \sum_{j=1}^m p_j |\Psi_j\rangle \langle \Psi_j| \]  

where \( \sum_{j=1}^m p_j = 1 \). The spectrum under the \( r \)-th measurement is given by

\[ S(\rho, r, x) = \sum_{j=1}^m p_j S(\Phi_j, \Phi_j, r, x) \]

In the standard Bell’s inequality, the experimentally measured correlation is defined as

\[ E(r, t) = \frac{N(+,+)}{N(+,+)} + \frac{N(-,-)}{N(-,-)} - \frac{N(+,-)}{N(+,-)} - \frac{N(-,+)}{N(-,+)} \]

where \( N(\cdot, \cdot) \) represents number of measurements yielding “+” in both measurement \( r \) and measurement \( t \) of channels I and II.

These measurement results are used to form the well-known Clauser-Horne-Shimony-Holt (CHSH) inequality (36)

\[ |E(r, t) + E(r, s) + E(q, s) - E(q, t)| \leq 2 \]

For continuous measurement results, we construct an auxiliary function \( V(r, t, x_1, x_2) \) to simplify calculating the correlation function \( E(r, t) \). The functional form of the auxiliary function can be found in the Supplementary Materials. The generalized standard Bell’s inequality for continuous variables takes the following form

\[ E = \frac{1}{\sqrt{2}} \int S(\rho, r, t, x_1, x_2) \frac{V(r, t, x_1, x_2) dx_1 dx_2}{dx_1 dx_2} \]

If this inequality (Eq. 11) is violated, then the system is entangled.

EXPERIMENTAL DESIGN

Recently, Zare and co-workers (30) reported the rotationally inelastic collisions between HD and HD, D₂ molecules at very low temperature. In their scattering experiments, the \( |H\rangle \) (orientation of molecules is parallel to their propagation direction) and \( |V\rangle \) states (orientation of molecules is vertical to their propagation direction) lead to very different scattering results, which offers us here a possible setup to classify entanglement between molecules based on the scattering results. In this section, we will propose an experimental setup to classify entanglement with continuous measurement results.

In the following simulations, we consider four measurements with respect to four different sets of eigenstate basis. The first one is the scattering measurements corresponding to eigenstates \( |H\rangle \) and \( |V\rangle \), which we note as measurement \( X \). The second one corresponds to the eigenstates \( |\pm\rangle = \frac{1}{\sqrt{2}}(|H\rangle \pm |V\rangle) \), which we note as measurement \( Z \). The other two measurements are taken with the \( Z_{X}\) and \( Z_{X-X} \) bases.

Measurement results in the \( Z \) basis could be taken from the experimental results of Zare and co-workers (30), which are continuous as a function of the scattering angles. We assume that the measurements in the \( X \) basis and \( Z_{X} \) are projection measurements, so that their results \( \Gamma \) are discrete, which is very common in the experimental setup. To check the derived inequality (Eq. 11), we assume that there is another scattering experiment for measurement \( Z_{X-X} \), whose results satisfy the Gaussian distribution. In Fig. 1, we show the ideal results (scattering angle \( \theta \) of measurement \( Z \) (upper part) and \( Z_{X-X} \) (lower part).

For our simulations, we start by preparing the oriented HD molecules \(|n=1, j=2, m=0\rangle\) in state \( |H\rangle \), whose orientation is parallel to its
The free parameter $p$ describes entanglement of the Werner state. $p = 0$ indicates separability, entanglement for $p \leq 1/3$, and Bell states of maximum entanglement at $p = 1$ (37).

If enough HD molecule pairs are prepared as mentioned above, then the predicted spectra for different initial states are shown in Fig. 3. The simulation is based on data of scattering experiment between HD and H$_2$ clusters taken from (30) (scattering spectrum; Fig. 4, A and B). We can calculate the density matrix $\rho_w$ for different measurements. For example, if both particles in channels I and II are scattered, then the measurement in the bases $|H\rangle$ and $|V\rangle$ gives

$$
\rho_w = \begin{pmatrix}
|HH\rangle & |HV\rangle & |VH\rangle & |VV\rangle \\
|HH\rangle & 1-p & 0 & 0 \\
|HV\rangle & 0 & 4 & 1+p \\
|VH\rangle & 0 & 2 & 0 \\
|VV\rangle & 4 & 0 & 1-p \\
\end{pmatrix}
$$

(13)

If we change the basis set, then the density matrix in the bases $|+\rangle$ and $|-\rangle$ gives

$$
\rho_w = \begin{pmatrix}
|++\rangle & |+-\rangle & |-+\rangle & |--\rangle \\
|++\rangle & 1+p & 0 & -p \\
|+-\rangle & 0 & 4 & 0 \\
|-+\rangle & 0 & 2 & 0 \\
|--\rangle & -p & 0 & 4 \\
\end{pmatrix}
$$

(14)

We could do the same expansion for different measurements. On the basis of Eq. 8, we can predict the results of different initial states, as shown in Fig. 3. The first column represents the simulation results when HD that goes through channel I is scattered, but not for channel II. The third column represents simulation results when HD that goes through channel II is scattered, but not for channel I. The last column represents results when particles are not scattered.

The state $|HH\rangle$ can be easily classified as its specific spectrum in the first column (Ch I, scattered; Ch II, scattered), and state $|++\rangle$ shows significant difference with others in the second (Ch I, scattered; Ch II, not scattered) and third columns (Ch I, not scattered; Ch II, scattered). For the Werner state, they share the same spectrum in the second and third columns, yet their spectrum in the last column (Ch I, not scattered; Ch II, not scattered) offers us some features: Counts for $S_1^+ S_2^-$ and $S_1^- S_2^+$ will decrease as $p$ increases. Also, the difference in the first column, where there is a subpeak (around $\theta_1 = 30, \theta_2 = 90$), increases when $p$ increases. On the basis of these features, it is possible to distinguish them from each other. However, if the initial state is a complex mixed state, then it is impossible for us to derive the initial state because there are infinite possible results of $\sum_{i=1}^{\infty} p_i |c_i(r, t, \pm\epsilon)|^2$ only with restriction $\sum_{i=1}^{\infty} p_i = 1$ and $\sum_{i=1}^{\infty} \pm |c_i(r, t, j_1, j_2)|^2 = 1$. However, with more information of $p_i$, there is a chance to resolve the quantum state. For example, if we have already known that the pairs are at the Werner state, then we could obtain the quantum state, as shown in the simulation work.
**MATERIALS AND METHODS**

Here, we show how to obtain the simulation results. As an example, we will take the first row in Fig. 3 (state $|\text{HH}\rangle$): channel I, scattered; channel II, scattered). Consider the HD molecule that goes through channel I. If the molecule HD scatted with a probability $P_{\text{scatter}}$, then the random number generator (RNG), where we assume that the RNG produces random numbers with uniform distribution, produces a number $a_1$, $0 \leq a_1 \leq 1$. If $a_1 \leq P_{\text{scatter}}$, then this HD molecule with a specific state will collide with $\text{H}_2$ clusters; otherwise, it will be measured by the gray sensor as shown in Fig. 2. For the scattered HD molecules, the specific prepared state will go through two channels, molecule in channel I will scatter with $\text{H}_2$ clusters, where the bond axis of $\text{H}_2$ is distributed isotropically. (C) Sensors (orange) are used to detect scattered particles and count numbers for each angle ($Z$ measurement). Molecules that are not scattered will go to another sensor (gray), by which they will be measured on the eigenstates $|+\rangle$ and $|−\rangle$ ($X$ measurement). (D) In channel II, we set another experiment, so that scattered prepared HD molecules with isotropically distributed $\text{H}_2$ clusters are measured under $\frac{Z+X}{\sqrt{2}}$, while the others are measured under $\frac{Z−X}{\sqrt{2}}$. 

**Fig. 2. Sketch of the experiment design.** (A) HD molecules are prepared in the state $|\nu=1, j=2, m=0\rangle$ using Stark-induced adiabatic Raman passage (SARP) (30). Then, we can divide them into two molecular beams (two groups). If we apply the Pumps and Stokes electric field along the $y$ axis, then HD in group I is set at state $|H\rangle$ (orientation of HD is along the $y$ axis, parallel to the direction of its propagation). The molecule HD in group II is set at state $|V\rangle$ (orientation of HD is along the $z$ axis, norm to the direction of its propagation). One molecule from group I and another from group II are combined together, and then, HD pairs are prepared at different initial states (if we do nothing, then these pairs will stay on a mixed state $|H\rangle \otimes |V\rangle$). (B) The specific prepared state will go through two channels, molecule in channel I will scatter with $\text{H}_2$ clusters, where the bond axis of $\text{H}_2$ is distributed isotropically. (C) Sensors (orange) are used to detect scattered particles and count numbers for each angle ($Z$ measurement). Molecules that are not scattered will go to another sensor (gray), by which they will be measured on the eigenstates $|+\rangle$ and $|−\rangle$ ($X$ measurement). (D) In channel II, we set another experiment, so that scattered prepared HD molecules with isotropically distributed $\text{H}_2$ clusters are measured under $\frac{Z+X}{\sqrt{2}}$, while the others are measured under $\frac{Z−X}{\sqrt{2}}$. 

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the scattering spectrum (measurement distribution) is \( f_H(\theta) \), as shown in Fig. 1, where \( \theta \) represents scattering angles, and we can get \( f_H(\theta) \) by fitting the results in the experimental measurements of Zare and co-workers (30). If the HD molecule at state \( |H\rangle \) is scattered, then the following process is used to generate its scattering angle: A random angle \( 0 \leq \theta \leq 180 \) and a random number \( a_2, 0 \leq a_2 \leq 1 \) are produced by RNG. If \( a_2 \leq f_H(\theta) \), then we accept \( \theta \) as the scattering angle; otherwise, this process is repeated. For the molecules that are not scattered, as \( |H\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |--\rangle) \), the measurement result has half possibility to be \( S_+ \) and another half to be \( S_- \). We can use one random number to simulate the measurement results of these unscattered molecules.

**DISCUSSION AND CONCLUSION**

In the measurement setting of the Werner state, Eq. 11 is violated when \( p > \frac{1}{2} \). Meanwhile, we know that the Werner state will be an entangled state when \( p > \frac{1}{2} \). Hence, violation of Eq. 11 guarantees existence of entanglement, yet the nonviolation of the inequality does not exclude the possibility of entanglement.
As shown in Fig. 4, the simulation result (red) $E$ is very close to the theory result (black). The difference is mostly due to the statistical error (please refer to the Supplementary Materials for method in simulation). We studied $1 \times 10^6$ particles and divided scattering angles into 18 slots ($10^\circ$ per slot). We studied $1 \times 10^6$ particles in simulation, and possibility to be scattered is set as 0.4.

In summary, we have generalized the standard Bell’s inequality from discrete to continuous measurement results. We designed an experimental setting as a potential application of violating the Bell’s inequality. We performed theoretical simulations to show the validity of the proposed experiment. The method is general and might be used to design and classify entanglement in new molecular scattering experiments.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/8/eaax5283/DC1

Section 5A. Bell’s inequality for continuous measurement results

Section 5B. Details of the simulation method

Section SC. An example of spin $\frac{1}{2}$ particles

Fig. S1. Sketch of Bell’s experiment of spin $\frac{1}{2}$ particles.

Fig. S2. Simulation result (122z).

Fig. S3. Simulation result (12zx).

Fig. S4. Simulation result (1x2z).

Fig. S5. Simulation result (1x2x).

Fig. S6. Simulation result (Werner state, $p = 0.6$).

References (38–40)
35. O. Rudolph, Computable cross-norm criterion for separability. *Lett. Math. Phys.* **70**, 57–64 (2004).

36. J. F. Clauser, M. A. Horne, A. Shimony, R. A. Holt, Proposed experiment to test local hidden-variable theories. *Phys. Rev. Lett.* **23**, 880 (1969).

37. R. F. Werner, Quantum states with Einstein-Podolsky-Rosen correlations admitting a hidden-variable model. *Phys. Rev. A* **40**, 4277 (1989).

38. M. Horodecki, P. Horodecki, R. Horodecki, Separability of n-particle mixed states: Necessary and sufficient conditions in terms of linear maps. *Phys. Lett. A* **283**, 1–7 (2001).

39. J. Lee, M. S. Kim, Entanglement teleportation via werner states. *Phys. Rev. Lett.* **84**, 4236 (2000).

40. Y. Yeo, Teleportation via thermally entangled states of a two-qubit heisenberg XX chain. *Phys. Rev. A* **66**, 062312 (2002).

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