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Quantum entanglement between electronic and vibrational degrees of freedom in molecules

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We consider the quantum entanglement of the electronic and vibrational degrees of freedom in molecules with tendencies towards double welled potentials. In these bipartite systems, the von Neumann entropy of the reduced density matrix is used to quantify the electron-vibration entanglement for the lowest two vibronic wavefunctions obtained from a model Hamiltonian based on coupled harmonic diabatic potential-energy surfaces. Significant entanglement is found only in the region in which the ground vibronic state contains a density profile that is bimodal (i.e., contains two separate local maxima). However, in this region two distinct types of density and entanglement profiles are found: one type arises purely from the degeneracy of energy levels in the two potential wells and is destroyed by slight asymmetry, while the other arises through strong interactions between the diabatic levels of each well and is relatively insensitive to asymmetry. These two distinct types are termed fragile degeneracy-induced entanglement and persistent entanglement, respectively. Six classic molecular systems describable by two diabatic states are considered: ammonia, benzene, BNB, pyridine excited triplet states, the Creutz-Taube ion, and the radical cation of the “special pair” of chlorophylls involved in photosynthesis. These chemically diverse systems are all treated using the same general formalism and the nature of the entanglement that they embody is elucidated. © 2011 American Institute of Physics. [doi:10.1063/1.3671386]

I. INTRODUCTION

Entanglement is one of the quintessential “quantum” phenomena. Here, we develop an understanding of the quantum entanglement between electrons and nuclei in molecules by an analysis of a simple model involving two coupled intersecting potential-energy surfaces. Such a system was first introduced by Horiuti and Polanyi in 1935 to describe proton and hydrogen transfer reactions1 and was subsequently extended by Hush to oxidation-reduction processes2 in 1953, now forming the basis of modern electron-transfer theory.3–6 describing for example exciton and charge transport through molecules, organic conductors and organic photovoltaics as well as electron-transfer reactions in biochemistry.7–18 It also describes general racemization processes19, 20 and has been widely used in spectroscopic analyses,21–23 forming the core of Herzberg-Teller theory.24–26 Indeed, Bersuker has suggested that all chemical processes can be described in this way as a pseudo Jahn-Teller effect.26 These chemical processes cause the vibrational and electronic motions of the molecule to become entangled.

In quantum information theory, the simplest type of system is a bipartite pure state given by \(|\psi\rangle = \sum_{ij} c_{ij} |a_i\rangle |b_j\rangle\) where \(|a_1\rangle, |a_2\rangle, \ldots, |a_n\rangle\) and \(|b_1\rangle, |b_2\rangle, \ldots, |b_m\rangle\) form any orthonormal set of basis vectors for subsystem A and B, respectively. We consider these subsystems as the electronic and vibrational degrees of freedom of a molecule, and the entanglement is, qualitatively, a measure of the connection between them. While many, related, definitions of entanglement have been proposed (see, e.g., Refs. 28–30), the von Neumann entropy of the reduced density matrix is the most common method of quantifying this entanglement, and we apply it to gain understanding of entanglement in chemical systems.

The chemical model used involves the interaction of a doubly degenerate electronic state with a non-degenerate vibration \((E \otimes B)\), a Herzberg-Teller system that can be considered as a special case of Jahn-Teller Hamiltonian 24–26, 31 that normally involves the interaction of a doubly degenerate electronic state with a doubly degenerate vibration \((E \otimes E)\). Such an approach can be used to describe molecules with symmetric double-welled potential-energy surfaces such as that observed for ammonia as a function of its inversion vibrational coordinate, as well as those observed for say inversion of molecular stereochemistry. In symmetric systems the diabatic potential-energy surfaces depicting the two localized wells have the same force constants and energy. We also consider pseudo \(E \otimes B\) systems in which an asymmetry \(E_0\) is introduced in the relative energies of the two wells, and the general scenario considered is sketched in Fig. 1. In this figure, the red and blue dashed curves represent diabatic potential-energy surfaces describing two non-interacting wells that are coupled by a resonance energy \(J\). These give rise to the classic Born-Oppenheimer ground-state adiabatic potential-energy surface and its

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associated excited state shown in purple and green in this figure, respectively.

We consider the properties of six molecular examples pertaining to this Hamiltonian: ammonia, BNB, benzene, the Creutz-Taube ion (CT), the bacterial photosynthetic center radical cation (PRC), and pyridine excited triplet states (3PYR), see Fig. 2 and Table I. These systems display a wide range of chemical and physical properties. For ammonia and BNB, $2\lambda/J$ is less than the reorganization energy $\lambda$ required to distort the molecule in one well to the nuclear coordinates of the minimum of other well (see Fig. 1) and so the Born-Oppenheimer surface is double welled. In contrast, for benzene the opposite is true, producing aromaticity with the carbon-carbon bonds taking on equal lengths rather than the alternating single-bond and double-bond pattern expected for Kekulé structures.

The precise nature of the Creutz-Taube ion has been debated for over 40 years, this molecule being the first mixed-valence compound investigated for which it was apparent that the molecule cannot be simply described as comprising an ion in each of two standard valence states (i.e., an Ru(II) and an Ru(III)), and this molecule became the paradigm through which biological electron transfer processes including those involved in solar-energy conversion during photo-synthesis was subsequently interpreted. Molecules showing these types of effects are often classified under the Robin-Day system as either Class II (localized double well), Class III (delocalized single well), or Class II–III (some mixture). Solar to electrical energy conversion occurs in the PRC when the “special pair” of bacteriochlorophylls shown in Fig. 2 ejects an electron to become a dimer radical cation. This ion can be thought of as a “mixed-valence complex” in which each bacteriochlorophyll could take the charge 0 or +1, and, like CT, the charge could alternatively be delocalized over both functionalities. Energy asymmetry in the PRC is induced naturally through asymmetric coordination with the surrounding protein as well as for the asymmetric protein electric field. The excited states of pyridine also display asymmetry but in this case its cause is chemical in origin as nitrogen substitution for CH in benzene makes the associated localized structures inequivalent. While this modifies the force constants of the diabatic states as well as their energies, the effect of the energy variation is the most profound and it is realistic to neglect force-constant variations in a simple model description. This scenario is appropriate to a very wide range of excited-state molecular spectroscopy and photochemistry.

We consider only the coupling of electronic states through a single vibrational mode, though in general many modes could contribute to the coupling. In practical situations, generalization to multiple modes is typically straightforward and is essential in quantitative analyses. Nevertheless, the essential physics of electron-vibration interaction in molecules can very often be described by the basic one-mode model using appropriately chosen effective vibrational parameters. Actually, the one-mode model is a good approximation for most properties of three of the molecules considered herein: ammonia, BNB, and benzene. For the excited triplet states of pyridine, at least 6 modes and 3 electronic states (includes the crossing (n, π*) state) are required in a quantitative analysis, whilst for CT a continuum of solvent modes is critical and 4 electronic states with 70 modes have been used to model PRC. In all cases, some important molecular properties such as the shape, central frequency, and intensity of the characteristic intervalence electronic transition are known to be independent of the number of modes used in the analysis.

The simple model thus provides a useful general starting position for considering electron-vibration entanglement. The Hamiltonian also describes a superconducting qubit coupled to the resonant microwave mode in a cavity, sometimes called

![FIG. 1. The chemical model used to describe electron-vibration entanglement. Harmonic diabatic surfaces (blue and red dashed lines), located at minima separated by $2\delta$ in some generalized dimensionless vibrational coordinate with energy asymmetry $E_0$, are coupled by a resonance interaction $J$. The ensuing Born-Oppenheimer ground-state and excited-state adiabatic potential-energy surfaces are denoted by purple and green solid lines, respectively. The reorganization energy $\lambda$ is also indicated.](image1.png)

![FIG. 2. Some sample molecular systems with electronic states that can be described using two coupled diabatic potential-energy surfaces.](image2.png)
Table I. Estimates of parameters values for the coupled harmonic potential-energy surfaces of some different molecular systems, along with the deduced vibronic entanglements $S_0$ and $S_1$.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_0$(eV)</th>
<th>$\hbar \omega$(cm$^{-1}$)</th>
<th>$J$(eV)</th>
<th>$\lambda$(eV)</th>
<th>$2J/\lambda$</th>
<th>$\hbar \omega$</th>
<th>$E_0/\hbar \omega$</th>
<th>$S_0$</th>
<th>$S_1$</th>
<th>$dS_0/\hbar \omega$</th>
<th>$dS_1/\hbar \omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>0</td>
<td>1580</td>
<td>−11.0</td>
<td>27.5</td>
<td>0.80</td>
<td>0.006</td>
<td>0.45</td>
<td>0.45</td>
<td>−420</td>
<td>−420</td>
<td>−420</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>1564</td>
<td>−9.5</td>
<td>5.7</td>
<td>3.3</td>
<td>0.010</td>
<td>0.01</td>
<td>0.03</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>$^3$PYR (Ref. 39)</td>
<td>0.26</td>
<td>1620</td>
<td>−0.33</td>
<td>2.0</td>
<td>0.3</td>
<td>0.095</td>
<td>1.3</td>
<td>0.03</td>
<td>0.29</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>CT (Ref. 35)</td>
<td>0</td>
<td>800</td>
<td>0.35</td>
<td>0.87</td>
<td>0.80</td>
<td>0.089</td>
<td>0.37</td>
<td>0.59</td>
<td>−0.05</td>
<td>−0.05</td>
<td>−0.05</td>
</tr>
<tr>
<td>PRC (Ref. 40)</td>
<td>0.069</td>
<td>~980</td>
<td>−0.13</td>
<td>0.14</td>
<td>1.8</td>
<td>0.41</td>
<td>0.6</td>
<td>0.17</td>
<td>0.57</td>
<td>−0.10</td>
<td>−0.10</td>
</tr>
<tr>
<td>BNB (Ref. 32)</td>
<td>0</td>
<td>1800</td>
<td>−0.36</td>
<td>0.98</td>
<td>0.74</td>
<td>0.18</td>
<td>0.44</td>
<td>0.73</td>
<td>−0.007</td>
<td>−0.007</td>
<td>−0.007</td>
</tr>
</tbody>
</table>

$^a$Derived from experimental data. $^{31,37,102,103}$ see supplementary material.

$^b$Using full 3-state 2-electron model $S_0 = 0.67$ and $S_1 = 0.67$, see supplementary material.

$^c$Using full 5-state 4-electron model $S_0 = 0.03$ and $S_1 = 0.09$, see supplementary material.

$^d$This value corresponds to the vibrational frequency of the libration mode of water, which calculations indicate to be the primary carrier of the distortion.

As the vibronic coupling between the ground state and the singly excited state involving these orbitals should parallel that between this singly excited state and its associated doubly excited state. Hence three states, the ground state, the singly excited state, and the doubly excited state, all share the same strong vibronic coupling. Alternatively, the Kekulé distortion of benzene mixes the doubly degenerate HOMO and LUMO orbitals, and so 4 electrons experience the same vibronic coupling scenario, generating a strongly coupled network of 7 electronic states. However, for both of these systems it is possible to reduce the multi-state interactions to give an effective two-state model involving renormalized parameters that accurately reproduce the properties of the electronic ground state of the system, as demonstrated in supplementary material. In the main text we utilize only the resulting effective 2-state model. Significantly, the transformations from the full Hamiltonians, in which electronic and nuclear degrees of freedom are fully separated, to the effective two-state models mix the electronic and nuclear motions, thus generating entanglement. For these systems, we provide results for the full minimalistic multi-state models in supplementary material to demonstrate that the two-state descriptions of the entanglement to actually depict all significant qualitative properties.

To manifest the electron-vibration entanglement we expand the exact, entangled, wavefunctions of the system in terms of unentangled basis states expressed diabatically as a product of an electronic wavefunction, $\phi$, dependent only on electronic coordinates, $r$, and a nuclear wavefunction, $\chi$, dependent only on nuclear coordinates, $R$, i.e.,

$$|\psi_{CA}(r, R)\rangle = |\phi(r)\rangle |\chi(R)\rangle. \quad (1)$$

This representation of the vibronic wavefunctions is known as the crude-adiabatic approximation and differs from the Born-Oppenheimer approximation in that no nuclear dependence of the electronic wavefunctions is allowed (i.e., the same electronic wavefunctions are used for all geometries). Exact numerical wavefunctions for the full Hamiltonian are then obtained, using these crude adiabatic wavefunctions as a basis set, in the form

$$|\psi_{exact}(r, R)\rangle = \sum_{ij} C_{ij} |\phi_i(r)\rangle |\chi_j(R)\rangle \quad (2)$$

from which the von Neumann entropy of the reduced density matrix $S$ can be readily obtained as the electronic and vibrational basis sets are orthonormal.

Such entanglement $S$ has been previously quantified in detail for the vibronic ground state of this model for $E_0 = 0$, and some results in the adiabatic limit are also available for $E_0 \neq 0$. Here we examine in detail how the entanglement changes when $E_0 \neq 0$, as well as considering for the first time entanglement within the lowest-energy vibronic excited state. These results bring into prominence the existence of two distinct types of entanglement in the parameter space: entanglement that persists despite the introduction of asymmetry (persistent entanglement) and entanglement that disappears (fragile degeneracy-induced entanglement).

At the moment no simple relationship is known linking the amount of entanglement manifested in a quantum state and its usefulness as a basis for qubits in some device; despite this, entanglement is almost universally referred to as a useful quantum information resource. In principle, any amount of entanglement is sufficient to allow quantum states to be used in some device for quantum information processing. The actual amount of entanglement in any one state is not necessarily a good indicator of performance as a typical experiment could, for example, mix an initially unentangled ground-state wavefunction with an initially unentangled excited-state wavefunction to produce a maximally entangled state.

However, entanglement must be very insensitive to environmental disturbances, such as dynamic motion of the system.
surrounding solvent, for all relevant quantum states in order to minimize device errors. As variations in the environment can be modeled as providing fluctuations in $E_0$, sensitivity of the entanglement to the environment can be depicted in a generally useful way by considering $dS/dE_0$. Understanding the consequences of asymmetry is critical to any application of electron-vibration entanglement to quantum information processing or quantum information transport and will particularly influence the design of experimental apparatus and conditions used for measuring electron-vibration entanglement. An advanced description of such an apparatus has only been proposed to measure entanglement between the electronic states of pairs of ammonia molecules, but means for measuring related properties for large molecules and nanoparticles with strong environment interactions have been conceived. We determine the basic molecular properties required to make the entanglement insensitive to environment, thus indicating which systems are likely to be useful in practice.

Our results also allow a broad picture to be developed of the significance of entanglement to the understanding of basic chemical bonding and reactivity. The magnitude of vibronic coupling is related to the entanglement between the electrons and nuclei. While the magnitude of vibronic coupling cannot easily be compared between molecules, entanglement can be.

II. MODEL HAMILTONIAN AND ITS PARAMETERS

Expressed in terms of a localized diabatic electronic basis set $|\phi_1\rangle, |\phi_2\rangle$, the coupled harmonic diabatic surfaces can be written as a function of a single generalized dimensionless nuclear coordinate $Q$ as

$$
H(Q) = \begin{bmatrix}
\hbar \omega \frac{(Q + \delta)^2}{2} - \hbar \omega \frac{d^2}{dQ^2} & J \\
J & \hbar \omega \frac{(Q - \delta)^2}{2} + E_0 - \hbar \omega \frac{d^2}{dQ^2}
\end{bmatrix},
$$

whenever

$$\frac{\hbar \omega}{\Delta E} \ll 1,$n\)

i.e., the vibrational energy-level spacing is much smaller than the electronic energy-level spacing. This approximation yields the ground-state (GS) and excited-state (ES) electronic potential-energy surfaces shown in Fig. 1 as it allows the effect of the nuclear momentum operator on the electronic wavefunction to be ignored so that $H$ can simply be diagonalized parameterically as a function of the nuclear coordinates $Q$. For $E_0 = 0$, the curvatures of these surfaces at $Q = 0$ are given by

$$\frac{\partial^2}{\partial Q^2} E_{GS} = \hbar \omega \left( 1 - \frac{\lambda}{2|J|} \right)$$

and

$$\frac{\partial^2}{\partial Q^2} E_{ES} = \hbar \omega \left( 1 + \frac{\lambda}{2|J|} \right)
$$

so that the ground-state surface becomes double welled whenever $\frac{\lambda}{2|J|} < 1$.

The diabatic Hamiltonian Eq. (3) is not unique as all physical properties, including electron-vibration entanglement, are invariant to the rotation of the electronic basis set $|\phi_1\rangle, |\phi_2\rangle$ that produces

$$H' = RHR^T,$

where

$$R = \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}.$$
In particular, a rotation of the localized diabatic Hamiltonian (Eq. (3)) typically used to describe double-welled systems such as ammonia by $\theta = 45^\circ$ produces the delocalized diabatic Hamiltonian typically used by spectroscopists to describe the ground and excited states of aromatic molecules. The essential feature of such a diabatic transformation matrix is that its matrix elements are independent of the nuclear coordinate $Q$, unlike say the transformation to the Born-Oppenheimer adiabatic description of the problem.

While four parameters $E_0$, $\omega$, $J$, and $\delta$ are specified in Eq. (3), entanglement is independent of the absolute energy scale and hence we simplify the problem by considering only the three independent parameters $2J/\lambda$, $\hbar\omega/\Delta E$, and $E_0/\hbar\omega$. Descriptive parameter values for the iconic systems ammonia, BNB, benzene, CT, PRC, and $^3$PYR are given in Table I.

Figure 3 indicates the physical significance of the ratios $\hbar\omega/\Delta E$ and $2J/\lambda$ by plotting the diabatic and adiabatic potential-energy surfaces generated with $\hbar\omega/\Delta E = 0.1$, 1, or 10 and $2J/\lambda = 0.1$, 1, or 10, all at $E_0/\hbar\omega = 0$. As the shapes of the diabatic surfaces are not invariant to electronic-state rotation (Eq. (8)), we seek here a “best-possible” diabatic representation of the low-energy parts of the potential-energy surfaces. To do this, we evaluate the lowest 10 vibronic energy levels from the diabatic surfaces as a function of $\theta$ at each point in the plots shown in the figure, optimizing the angle to minimize the difference between these energy levels and those produced following full diagonalization of the coupled electron-vibration Hamiltonian (which are physical observables and hence independent of $\theta$). In Fig. 3, the vibrational levels of the lower-energy diabatic surface are indicated by blue solid lines, while the vibrational levels of the higher-energy diabatic surface indicated by red dashed lines; the optimized angles $\theta$ are also indicated.

An optimized angle near $\theta = 0^\circ$ indicates that fully localized states provide the best-possible diabatic description of the intersecting potential-energy surfaces. This result is produced whenever $\hbar\omega/\Delta E < 1$ and $2J/\lambda < 1$, roughly the region in which the ground-state adiabatic potential-energy surface is double-welled and supports below-barrier zero-point vibration. Optimized angles near $\theta = 45^\circ$ result whenever $\hbar\omega/\Delta E < 1$ and $2J/\lambda > 1$, the region in which the adiabatic potential-energy surfaces are well-separated from each other and are single well, typical, say, of the delocalized aromatic states of benzene. In the intermediate region with $\hbar\omega/\Delta E < 1$ and $2J/\lambda \sim 1$ the ground-state adiabatic potential-energy surface becomes flat and very anharmonic, leading to highly unusual molecular properties, e.g., for the Creutz-Taube ion. When $\hbar\omega/\Delta E > 1$, the scenario is that of well-separated vibrational levels split by small electronic effects, making the Born-Oppenheimer approximation a poor descriptor of system properties. In this regime, the optimum diabatic angle $\theta$ is no longer a physically significant indicator, and the effects of vibrations not included in the Hamiltonian may dominate any real chemical scenario, bringing into operation say the Jahn-Teller effect.

### III. NUMERICAL DETERMINATION OF THE HAMILTONIAN EIGENFUNCTIONS

To find converged numerical solutions to the eigenvectors of $H$, this operator is represented using a product basis of the form $\phi_i \otimes \chi_j$, with $\{\phi_1, \phi_2\}$ forming the (localized) diabatic electronic basis and $\{\chi_1, \chi_2, \ldots, \chi_n\}$ forming a truncated harmonic-oscillator vibrational basis centered around $Q = 0$. The Hamiltonian matrix elements are then given by

\[
\begin{align*}
H_{i,1j} &= H_{1,1i} = \langle \chi_i \phi_1 | H | \phi_1 \chi_j \rangle = -\delta \hbar \omega \sqrt{\frac{\lambda+1}{\lambda}} \delta_{j,i+1} + (i + \frac{1}{2}) \hbar \omega \delta_{i,j} \\
H_{i,2j} &= H_{2,2i} = \langle \chi_i \phi_2 | H | \phi_2 \chi_j \rangle = \delta \hbar \omega \sqrt{\frac{\lambda+1}{\lambda}} \delta_{j,i+1} + [E_0 + (i + \frac{1}{2}) \hbar \omega] \delta_{i,j} \\
H_{i,2j} &= H_{2,1i} = \langle \chi_i \phi_1 | H | \phi_2 \chi_j \rangle = J \delta_{i,j}
\end{align*}
\]
Diagonalizing the Hamiltonian matrix then allows 2n independent wavefunctions to be written in the form

$$|\psi_j\rangle = \sum_{i=1}^{n} c_{1i,j}|\phi_1\chi_i\rangle + c_{2i,j}|\phi_2\chi_i\rangle.$$  \hspace{1cm} (11)

In particular, we are interested in the properties of the ground-state vibronic wavefunction $|\psi_0\rangle$ and the wavefunction of next highest energy, $|\psi_1\rangle$.

IV. ENTANGLEMENT AS THE VON NEUMANN ENTROPY

The entanglement between the electronic and nuclear degrees of freedom can be expressed as the associated von Neumann entropy of the reduced density matrix, \cite{27,31} obtained by re-expressing the eigenfunctions from Eq. (11) in the form

$$|\psi_j\rangle = \sum_{k=1}^{2} \phi_k(q) \left[ \sum_{i=1}^{n} c_{ki,j}\chi_i(Q) \right] = \sum_{k=1}^{2} \phi_k(q)\chi_k(Q)$$

or

$$|\psi_j\rangle = \sum_{i=1}^{n} \left[ \sum_{k=1}^{2} c_{ki,j}\phi_k(q) \right] \chi_i(Q) = \sum_{i=1}^{n} \phi_j(q)\chi_i(Q).$$ \hspace{1cm} (11a)

where $q$ and $Q$ are the electronic and vibrational co-ordinates, respectively. Based on these expansions, reduced electronic and vibrational density matrices for eigenstate $j$ can be defined as

$$\rho_{E}^{j} = \int_{-\infty}^{\infty} \chi_{i}^{\dagger}(Q)\chi_{i}(Q)dQ = \sum_{i=1}^{n} c_{ki,j}c_{li,j}$$

and

$$\rho_{V}^{j} = \int_{-\infty}^{\infty} \phi_{j}(q)\phi_{j}(q) dq = c_{1i,j}c_{1i,j} + c_{2i,j}c_{2i,j}. $$ \hspace{1cm} (12)

While $\rho_{E}^{j}$ is a $2 \times 2$ matrix and $\rho_{V}^{j}$ is an $n \times n$ matrix, both share the same set of at-most-two non-zero eigenvalues $\rho_{\perp}$, and $\rho_{\perp} = 1 - \rho_{\perp}$ (with $0 \leq \rho_{\perp} \leq 1/2$). The commonality of these two eigenvalues can be seen by writing the quantum state as a Schmidt decomposition, which can have at most two terms. \cite{30} The von Neumann entropy of eigenstate $j$ can thus be expressed as

$$S_j = - \rho_{\perp} \log_{2} \rho_{\perp} - (1 - \rho_{\perp}) \log_{2}(1 - \rho_{\perp}).$$ \hspace{1cm} (13)

If $\rho_{\perp} = 0$, the wavefunction can be expressed as a single product of an electronic wavefunction and a vibrational wavefunction and as a result there is no entanglement, $S_j = 0$. Alternatively, if $\rho_{\perp} = 1/2$, the wavefunction is maximally entangled and $S_j = 1$. It is hence convenient to express the two eigenvalues as

$$\rho_{\perp} = \frac{1}{2}(1 - \Delta \rho^{j})$$

and

$$\rho_{\perp} = (1 - \rho_{\perp}) = \frac{1}{2}(1 + \Delta \rho^{j}).$$ \hspace{1cm} (14)

The entanglement within eigenstate $j$ is then maximal when $\Delta \rho^{j} = 0$ and minimal when $\Delta \rho^{j} = 1$.

V. FRAGILE VS. PERSISTENT ENTANGLEMENT

The entanglements $S_0$ for the ground vibronic-state wavefunction and $S_1$ for the first-excited vibronic-state wavefunction are shown in Fig. 4, calculated over the whole parameter space of the model Hamiltonian. For symmetric systems ($E_0 = 0$), the entanglement is large whenever $2|J| < \lambda$ and $\Delta E > \hbar \omega$. From Fig. 3 it is clear that this region corresponds to double-well potentials that support localized vibrational motions.

However, Fig. 4 also shows that the introduction of a small amount of asymmetry, manifest at say $E_0/\hbar \omega = 0.01$, results in a dramatic reduction of the ground-state entanglement, with significant entanglement becoming restricted predominantly to a region within 0.02 $< 2|J|/\lambda < 0.5$ and 0.1 $< \hbar \omega/\Delta E < 1$. The entanglement that remains at $E_0/\hbar \omega = 0.01$ is said to be persistent whilst that which is lost is said to be degeneracy-induced entanglement. After the initial dramatic reduction in the ground-state entanglement for small values of $E_0/\hbar \omega$, the entanglement continues to decrease slowly with increasing asymmetry. The greatest entanglement becomes concentrated in the regions near $2|J|/\lambda$ just less than 1 and $\hbar \omega/\Delta E$ values of 0.3 for $E_0/\hbar \omega = 0.1, 0.2$ for $E_0/\hbar \omega = 0.6$ and 0.1 for $E_0/\hbar \omega = 1.3$, with always a tail extending to low $E_0/\hbar \omega$ for $2|J|/\lambda = 1$. Similar results have also been observed using adiabatic calculations on a qubit coupled to an oscillator \cite{59} and in applications of the spin-boson model. \cite{73,74} The feature that we stress here is that while asymmetric systems inherently manifest less entanglement in the ground-state wavefunction than do symmetric double-welled systems, the sensitivity of this entanglement to external perturbations is much less than that which symmetric systems can sometimes develop.

The fragility of the degeneracy-induced entanglement can be understood by expanding the non-zero eigenvalues of the density matrices for the ground state and first vibronic excited state using perturbation theory in the localized limit of $2|J|/\lambda \ll 1$, giving

$$\Delta \rho^{0} = \Delta \rho^{1} = \left( 1 - \frac{1 - F_{00}}{1 + E_0/(2|J|F_{00})} \right)^{1/2},$$ \hspace{1cm} (15)

where

$$F_{00} = \exp \frac{-\lambda}{2\hbar \omega},$$ \hspace{1cm} (16)

is the Franck-Condon overlap of the two localized-well harmonic-oscillator diabatic ground-state functions, see supplementary material. \cite{56} Note that these equations actually remain useful to even up to at least $2|J|/\lambda = 0.5$. As ground-state entanglement is large whenever $\Delta \rho^{0} < 1$, significant entanglement can only occur whenever

$$E_0 < 2|J|\exp \frac{-\lambda}{2\hbar \omega},$$

or

$$\frac{E_0}{\hbar \omega} < \frac{2|J|/\lambda}{\Delta E} \exp \frac{-\Delta E}{2\hbar \omega}. $$ \hspace{1cm} (17)

This equation indicates that $E_0/\hbar \omega$ is maximized when $\hbar \omega/\Delta E = 1/2$ and when $2|J|/\lambda$ is maximized, qualitatively explaining the results presented in Fig. 4 for $2|J|/\lambda < 1$,.
for example the maximum entanglement at $E_0/\hbar\omega = 0.01$ in Fig. 4 occurs near $2|J|\lambda = 0.1$, $\hbar\omega/\Delta E = 0.3$ at which point the right-hand side of Eq. (17) evaluates to 0.005–0.01. In any practical scenario, the entanglement of the eigenfunctions in a symmetric system will be robust to environmental fluctuations only if these are very much less that the oscillator frequency, demanding high-frequencies and/or very low temperatures, and the symmetric double well must support a minimum number of locally bound vibrational levels.

A very rapid change occurs in the nature of the eigenvectors of $H$ occurs as $2|J|\lambda$ increases towards unity and as a result for $2|J|\lambda \geq 1$ the extreme sensitivity of the entanglement to $E_0$ is lost and the entanglement remains persistent. In this region of the parameter space, the eigenvalues of the ground-vibronic-level density matrix can be expanded using perturbation theory based on the delocalized diabatic Hamiltonian and through Eq. (14) become specified by

$$\Delta \rho^0 = 1 - \frac{\hbar\omega}{2(\hbar\omega - 2|J|)^2(1 + E_0^2/16J^2)}.$$  

This expression is exact in the limit $2|J|\lambda \gg 1$. As the entanglement becomes large whenever $\Delta \rho^0 \ll 1$, this equation indicates that $\rho_0 \to 2|J| \sim \Delta E$ will maximize entanglement whenever $2|J|\lambda > 1$, as indicated in Fig. 4. Asymmetry $E_0$ damps this entanglement for large values of $\hbar\omega/\Delta E$ but whenever $(E_0/\hbar\omega)^2 \ll 4(\hbar\omega/\Delta E)^2$ the entanglement becomes insensitive to asymmetry, e.g., for $\hbar\omega/\Delta E \ll 1$,

$$S_0S_1 \sim -\rho_0 \log_2 \rho_0,$$

where

$$\rho_0 = \left(1 + \frac{\lambda}{2|J|} \frac{\hbar\omega}{\Delta E} \left(1 + \frac{\lambda}{2|J|}\right)\right).$$

This explains the very rapid attenuation of the entanglement shown in Fig. 4 as $2|J|\lambda$ increases above unity for small $\hbar\omega/\Delta E \ll 1$ whilst also indicating how the very fragile entanglement shown for $2|J|\lambda$ just less than unity quickly turns into persistent entanglement.

Also shown in Fig. 4 are the Born-Oppenheimer potential-energy surfaces at a salient point in the parameter space for each illustrated value of $\Delta E/\hbar\omega$, along with the vibrational densities calculated from the exact wavefunctions at these points: for $E_0 = 0$, the point at $2|J|\lambda = 0.1$, $\hbar\omega/\Delta E = 0.1$ in the strongly entangled region is illustrated, whilst for $E_0 \neq 0$ the points manifesting the largest ground-state entanglement are selected. The selected points for both $E_0/\hbar\omega = 0$ and 0.01 display double-welled potential-energy surfaces that are sufficiently deep to support zero-point vibration and thus generate bimodal density profiles (i.e., have a local minimum in the density at or near $Q = 0$ separating two local maxima).

The entanglement $S_0$ at each of these points is also large, exceeding 0.93. However, the parameters that maximize the entanglement for $E_0/\hbar\omega \geq 0.1$ all result in unimodal ground-state density profiles indicating that the wavefunctions have become localized into the lower-energy diabatic well. At $E_0/\hbar\omega = 0.1$, the entanglement remains significant, $S_0 = 0.67$, but this reduces quickly as $E_0/\hbar\omega$ increases, becoming just $S_0 = 0.16$ at $E_0/\hbar\omega = 1.3$. 

FIG. 4. Persistent versus degeneracy-induced entanglement. Center and right: Electron-nuclear entanglement (von Neumann entropy) is bimodal or unimodal, while the crosses in-

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In Fig. 4, the regions in which the ground-vibronic-state density is bimodal are indicated and can be seen to correspond to regions in which the entanglement is in excess of \( \sim 0.7 \). This is true at both \( \bar{\omega} / \hbar \omega = 0 \), encompassing both persistent and fragile entanglement, and at \( \bar{\omega} / \hbar \omega = 0.01 \) for which only persistent entanglement of this magnitude remains. Hence we see that regions of fragile entanglement are also the regions in which bimodal density profiles become unimodal after the application of very small asymmetries. This qualitative change associated with the unimodal-bimodal changeover has some similarities to a quantum phase transition in a system with an infinite number of degrees of freedom.\(^{77}\) Consideration of the density thus provides a possible means for understanding entanglement within the ground vibronic wavefunction. Similar results occur in other types of qubits, see, e.g., Refs. 29, 42, 78–90. In particular, systems in which bimodal density profiles survive finite temperature\(^{65,91}\) are clearly ones in which the entanglement is persistent.

For the first excited-state vibronic level, the overall effect is similar to that for the ground vibronic state but the region of persistent entanglement is much larger and survives beyond \( \bar{\omega} / \hbar \omega = 1 \). For the symmetric double-well situation with \( \bar{\omega} / \hbar \omega = 0 \) and \( 2J / \lambda < 1 \), the first excited vibronic eigenfunction is very similar to the associated ground-state function except for the opposite phasing of the two localized-diabatic ground states, and so the entanglements \( S_0 \) and \( S_1 \) behave very similarly in this region: Eq. (16) again depicts the origin of fragile symmetry-induced entanglement when \( \bar{\omega} / \hbar \omega < 0.1 \), while Eq. (19) again shows how the entanglement diminishes in magnitude but becomes persistent as soon as \( 2J / \lambda > 1 \) exceeds unity. However, the similarity between the behavior of \( S_0 \) and \( S_1 \) is lost when \( \bar{\omega} / \hbar \omega \) approaches 1, as in this scenario the localized diabatic ground-state from one well becomes degenerate with the localized first excited level of the other, as illustrated in Fig. 5. As a result, \( S_1 \) remains large at all values of \( \bar{\omega} / \hbar \omega \), being large in the limit of \( 2J / \lambda \gg 1 \) whenever

\[
\left( \frac{E_0}{\bar{\omega}} \right)^2 + \left( \frac{2J}{\hbar \omega} \right)^2 \approx 1. \quad (20)
\]

This equation also indicates the effects of an additional resonance that occurs in the delocalized diabatic limit at \( 2J / \hbar \omega = 1 \) in which the first excited vibrational level of the ground delocalized state equals the zero-point level of the excited delocalized state; this gives rise to the large persistent entanglement near \( \hbar \omega / \Delta E = 1 \) for \( 2J / \lambda > 1 \), see Fig. 5.

\[ \text{FIG. 5. Origin of the resonances that enhance entanglement } S_1 \text{ in the first excited vibronic state: left—crude adiabatic surfaces at } E_0 / \omega = 1 \text{ and } \hbar \omega / \Delta E = 0.1 \text{ at } \theta = 0 \text{ and right—crude adiabatic surfaces at } \hbar \omega / \Delta E = 1 \text{ and } 2J / \lambda = 10 \text{ at } \theta = 45^\circ. \]

VI. RELATION TO THE BOHM-AHARONOV TEST OF THE EINSTEIN-PODOLSKY-ROSEN PARADOX

The Einstein-Podolsky-Rosen paradox\(^{92}\) involves a pair of entangled states of continuous variables (position and momentum). Bohm and Aharonov\(^{93,94}\) re-formulated a test of the EPR paradox in terms of discrete degrees of freedom, a pair of singlet-coupled spins. The chemical systems considered are intermediate between EPR and Bohm-Aharonov because one degree of freedom is discrete (the two state electronic system) and the other involves a continuous degree of freedom (the vibrational coordinate). For coupled spins, interactions with the environment destroy entanglement by “measuring” the spin state, whereas in a chemical system interactions with the environment destroy symmetry to prevent entanglement from ever developing; to do this in a Bohm-Aharonov experiment, the environment would need to provide a magnetic field strong enough to make a component of \(^3\)\(^1\)\(^2\) for the ground-state of the molecule to eliminate the entanglement. Dissociating a singlet state provides just one example of the general chemical effect of static electron correlation, the type of electron correlation that arises when symmetry rather than interaction determines key features of a quantum state.\(^{95}\) Static electron correlation can thus be a source of fragile degeneracy-based entanglement, entanglement that is destroyed by either weak intramolecular interactions or weak external fields that break the symmetry.

VII. APPLICATIONS TO SOME MODEL MOLECULAR SYSTEMS

The properties of the 6 paradigm molecular systems considered are listed in Table I, including the calculated values of the ground vibronic level entanglement \( S_0 \) and the first-excited vibronic level entanglement \( S_1 \); the appropriate molecular data points are also marked on Fig. 4. Ammonia, benzene, CT, and BNB all appear on the \( E_0 / \bar{\omega} \) = 0 diagram in Fig. 4 and are found reasonably close together, despite their qualitatively different chemical properties; this is indicative of the broad range of chemical systems that can be modeled. CT and BNB fall in a region of persistent entanglement, there being no significant change in \( S_0 \) and \( S_1 \) at \( E_0 / \bar{\omega} \approx 0.01 \) compared to \( E_0 / \bar{\omega} = 0 \) for these molecules, but the entanglements for ammonia decrease dramatically with this small amount of asymmetry. This effect is quantified in Table I in which the derivatives \( dS_0 / dl (E_0 / \bar{\omega}) \) are listed for each molecule: for the ground vibronic level, these are \(-0.050\) and \(-0.007\) for CT and BNB, respectively, but \(-420\) for ammonia. Indeed, the deduced sensitivity of the entanglement for ammonia indicates that, in any conceivable quantum device exploiting entanglement, robust operation will require an extreme level of environmental isolation. For benzene the entanglement is highly insensitive to environment but its magnitude is very small for both the ground and first-excited vibronic levels, \(<0.03\), and any practical quantum device would need to mix say the ground vibronic with some very high-energy level in order to generate significant entanglement. Intrinsically asymmetric systems such as \(^3\)PYR and PRC can generate significant entanglement with intermediate levels of...
environmental sensitivity and so in this respect are not fundamentally incompatible with the needs of a practical quantum device.

Isomerization in closed-shell molecules such as ammonia and benzene intrinsically generate multiple strongly interacting excited-state potential-energy surfaces, and, while it is possible to accurately represent the ground electronic state for these systems using effective two-state models, the transformation into this form is not diabatic and so generates additional entanglement between electronic and vibrational degrees of freedom not embodied in the two-state model. In supplementary material,56 we show the entanglements of the ground vibronic level and first excited vibronic levels calculated using multi-state models and compare them to those already shown in Fig. 4. While adding the additional coupled states introduces no significant qualitative changes, the region of persistent entanglement does become restricted even further towards the region around $2 |J| / \lambda \sim 1$ and $\hbar \omega / \Delta E \sim 1$, with a tail extending to low vibration frequency for $2 |J| / \lambda \sim 1$. Also, quantitatively changes to the entanglement near $2 |J| / \lambda \sim 1$ are identified, and this effect could not be ignored during accurate modeling of device properties.

Often it is possible to use chemical or spectroscopic means to modify the basic molecular parameters, opening up the possibility of dynamically switching entanglement on and off. CT not only presents the largest persistent entanglement of all the molecules considered but also allows for this possibility. X-ray photoelectron spectroscopy (XPS) can be used to create a core hole that, because of the small overlap between the core orbitals on the two Ru atoms, becomes 98% localized onto one of the two metal centers,33 introducing an asymmetry96 of $E_g = 22,000 \text{ cm}^{-1}$ making $E_g/\hbar \omega = 28$. The calculated entanglement for this switched CT is $S_1 = 0.0007$, a reduction by a factor of 500.

**VIII. CONCLUSIONS**

Double-welled chemical systems by their nature embody electron-vibrational entanglement, and the entanglement of the lowest-energy eigenfunctions is found to be largest when the ground-state wavefunction has a bimodal density profile, with each maximum depicting localization of the wavefunction on one side of the double well. Ammonia provides a typical example of this effect, displaying significant ground-state entanglement of 0.45 and a bimodal density profile, but its well is shallow and supports only 4 localized vibrational levels.97 Similar entanglement is also manifest by BNB and CT which have double wells but unimodal density profiles that display just one single maximum near or at the symmetric configuration. However, the entanglement does decrease rapidly when double-wells disappear altogether, falling to $<0.1$ for benzene. Truly asymmetric systems such as the special-pair radical cation in natural photosynthesis and the excited states of pyridine can also manifest significant entanglement.

While the degree of entanglement in the ground-state wavefunction provides important information concerning its nature, the sensitivity of the entanglement to environmental fluctuations is a critical indicator of the suitability of a molecule in some proposed quantum device. Symmetric systems are shown to possess two types of entanglement, fragile entanglement that is lost in the presence of small environmentally induced asymmetries and persistent entanglement that is robust to such effects. The sensitivity of the entanglement to environment is found to range over 7 orders of magnitude for the chemical systems considered, being extremely small for benzene and extremely large for ammonia. This effect can have significant consequences in devices that utilize these wavefunctions. For example, mixing of the ground and first-excited vibronic levels in ammonia has been suggested62 as the basis of a qubit in a quantum device, the instantaneous state of such a qubit being of the form

$$\Psi = a |\psi_0\rangle + b |\psi_1\rangle = \sum_{i=1}^{n} (ac_{i1,0} + bc_{i1,1})|\phi_{1i}\rangle + (ac_{2i,0} + bc_{2i,1})|\phi_{2i}\rangle.$$  

(21)

Sensitivity of the electron-vibration entanglement within each state to environment indicates that the contributions $c_{1i,0}$ etc. are highly sensitive to environmental fluctuations and therefore so is the quantum state of the proposed qubit. This is an undesired feature that would demand extreme levels of isolation of the qubit from its environment (as happens say in dilute gasses and utilized in the ammonia maser) but is unlikely in any solid-state device. However, BNB is shown to provide a simple chemical system akin to ammonia for which the ground-state entanglement is large and persistent, suggesting that this may be a useful candidate molecule for use in a quantum device. Nevertheless, this molecule does not have parameters in the optimal range of $0.02 < 2|J|/\lambda < 0.5$ and $0.1 < \hbar \omega / \Delta E < 1$ and so improved molecular candidates should be sought before any quantum device is implemented. Interestingly, large molecular systems such as CT and PRC show both significant ground-state entanglement and low environmental sensitivity, indeed utilizing environmental interactions to generate the vibronically active models that would actually be exploited in a quantum device. Entanglement is known to be able to persist in such environments63, 65, 67, 91 and so they cannot be trivially eliminated as candidate systems for quantum devices. Further, we describe a spectroscopic method by which entanglement could be switched on and off for CT, a useful feature in any device.

Entanglement of the first vibrational level occurs over much the same region of the parameter space as does entanglement of the ground state and shows similar environmental sensitivity, developing from the oppositely phased linear combination of the localized-well zero-point vibrations, but also occurs in a much larger region of the parameter space owing to specific new resonances involving locally excited vibrations. While resonance-driven entanglement is persistent, its manifestation would be much more difficult for most systems and also it would be sensitive to the multi-modal nature of real molecular motions.

Fragile entanglement in ammonia is indicative of the basic chemical properties of this molecule which has often been used as a model for complex chemical phenomena.
such as charge and energy transfer through symmetric double wells.\cite{Marcus1960, Hush1957} The effect of minute asymmetry in blocking coherent charge and energy transport has been described\cite{Marcus1956} and can be considered as occurring as a consequence of fragile entanglement, as can effects associated with environmentally induced asymmetry in electronic states dominated by static electron correlation. Thus, there appears an intrinsic time entanglement, as can effects associated with environment must persist so that the transport obeys quantum rather than classical laws.

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\begin{thebibliography}{100}
\bibitem{N. Sh. Hush, Polyom. Sci. 11, 289 (1953).
\bibitem{R. A. Marcus, Discuss. Faraday Soc. 21 (1960).
\bibitem{See supplementary material at http://dx.doi.org/10.1063/1.3671386 for the derivation of Eq. (15) and a description of the 3-state and 5-state extended vibronic coupling models for closed-shell reactions, their reduction to effective 2-state models, parameter determinations for ammonia and benzene based on experimental data, and the differences between the entanglements manifest by the full models and their effective 2-state approximations.
\bibitem{M. Born and R. Oppenheimer, Ann. Phys. 84, 457 (1927).
\bibitem{H. B. Bersuker, The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry (Springer, New York, 1984).