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Quantum superpositions in photosynthetic light harvesting: delocalization and entanglement

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Abstract. We explore quantum entanglement among the chlorophyll molecules in light-harvesting complex II, which is the most abundant photosynthetic antenna complex in plants containing over 50% of the world’s chlorophyll molecules. Our results demonstrate that there exists robust quantum entanglement under physiological conditions for the case of a single elementary excitation. However, this nonvanishing entanglement is not unexpected because entanglement in the single-excitation manifold is conceptually the same as quantum delocalized states, which are the spectroscopically detectable energy eigenstates of the system. We discuss the impact of the surrounding environments and correlated fluctuations in electronic energies of different pigments upon quantum delocalization and quantum entanglement. It is demonstrated that investigations with tools quantifying the entanglement can provide us with more detailed information on the nature of quantum delocalization, in particular the so-called dynamic localization, which is difficult for a traditional treatment to capture.
1. Introduction

In 1944, Schrödinger published a short volume entitled *What is Life?* [1] summarizing the emerging molecular aspects of biology at that time from his perspective. The book spearheaded the rise of molecular biology and thus had a tremendous impact on the development of 20th-century biology. One of the fundamental questions that he raised was whether quantum mechanics could be a key feature for explaining biological phenomena. Six decades later, there is still considerable debate on whether quantum mechanics plays significant and nontrivial roles in biological organisms [2], aside from well-understood quantum phenomena such as chemical bonding.

However, recent experiments using two-dimensional electronic spectroscopy [3]–[7] have clearly revealed that electronic energy transfer (EET) in photosynthetic light harvesting involves long-lived quantum coherence among electronic excitations of pigments. The observed coherence implies that electronic excitations of pigments travel through photosynthetic proteins as quantum wave packets keeping their phase coherence, rather than by incoherent diffusive motion following classical rate laws. The existence of long-lived quantum coherence in noisy environments, such as proteins, has attracted the attention of researchers in the field of quantum computation and information science, because avoidance of decoherence is a crucial factor for quantum information processing [8]. Recent investigations have addressed nonclassical correlations [9]–[15] such as quantum entanglement in photosynthetic pigment–protein complexes (PPCs). Quantum entanglement, originally discussed by Schrödinger [16], implies ‘spooky’ nonlocal correlation inherent to quantum mechanics and hence caused skepticism in the early days of quantum mechanics [17]. In the current era, however, entanglement is regarded as an indispensable resource to performing nontrivial computation and communication tasks that are impossible to do in a classical manner [8].

In this paper, we explore quantum entanglement among the pigments in light-harvesting complex II (LHCII). LHCII is the most abundant photosynthetic antenna complex in plants containing over 50% of the world’s chlorophyll molecules [18]. As depicted in figure 1, the complex is a trimeric system composed of three monomeric subunits arranged with $C_{3v}$ symmetry. Each subunit contains 14 chlorophyll molecules with two spectral variants, eight chlorophyll $a$ (Chl$a$) molecules producing an absorption band from 14 500 to 15 000 cm$^{-1}$, and six chlorophyll $b$ (Chl$b$) molecules giving rise to an absorption peak around 15 500 cm$^{-1}$ [5, 19]. It has been shown that LHCII also exhibits long-lived quantum coherence [5]. Through
Figure 1. The crystal structure of LHCII isolated from spinach [20]. The relative position of the chlorophylls (Chl a in green and Chl b in blue) is drawn with the α-helices spanning the membrane. (a) The trimeric LHCII viewed from the stromal side. (b) Side view of a monomeric unit.

discussions on the quantum entanglement in LHCII, we also analyze the influence of the surrounding environment on quantum entanglement in a more detailed fashion.

2. Modeling of LHCII

In this paper, we assume that the inter-subunit coupling is vanishingly small and we consider the EET within one monomeric subunit illustrated in figure 1(b). To describe EET in LHCII, we restrict the electronic spectrum of the $m$th chlorophyll ($m = 601–614$, enumeration from the x-ray structure [20]) to the ground state $|\psi_{mg}\rangle$ and the first excited state $|\psi_{me}\rangle$, namely we treat 14 qubits. There exists no experimental evidence of nonadiabatic transitions and radiative/nonradiative decays between $|\psi_{me}\rangle$ and $|\psi_{mg}\rangle$ in LHCII on the picosecond timescales discussed in this work [19, 21]. Thus, the PPC Hamiltonian can be expressed as [22, 23]

$$H_{PPC} = H_{el} + H_{ph} + H_{el-ph}. \quad (1)$$

The first part $H_{el}$ is the Hamiltonian describing the electronic transition expressed as

$$H_{el} = \sum_{m} \hbar \Omega_{m} B_{m}^\dagger B_{m} + \sum_{m \neq n} \hbar J_{mn} B_{m}^\dagger B_{n}, \quad (2)$$

where $\hbar \Omega_{m}$ is the Franck–Condon energy defined as the optical transition energy at the equilibrium configuration of environmental phonons associated with the ground state, and $\hbar J_{mn}$ denotes the excitonic coupling between the $m$th and $n$th chlorophylls. In equation (2), creation and annihilation operators have been introduced as $B_{m}^\dagger = |\psi_{me}\rangle \langle \psi_{mg}|$ and $B_{m} = |\psi_{mg}\rangle \langle \psi_{me}|$, respectively, where we postulate the anti-commutation relations, $\{B_{m}^\dagger, B_{n}\} = \delta_{mn}$, $\{B_{m}^\dagger, B_{m}^\dagger\} = 1$, and $\{B_{m}, B_{n}\} = (1 - \delta_{mn})2B_{m}^\dagger B_{n}$ and $\{B_{m}^\dagger, B_{n}\} = (1 - \delta_{mn})2B_{m} B_{n}^\dagger$ [24, 25]. Here, the relation $\{B_{m}^\dagger, B_{m}\} = |\psi_{mg}\rangle \langle \psi_{mg}| + |\psi_{me}\rangle \langle \psi_{me}| = 1$ is interpreted as the completeness relation for the electronic state of the $m$th pigment, whereas the equality $\{B_{m}^\dagger, B_{m}^\dagger\} = 2B_{m}^\dagger B_{m}^\dagger = 0$ indicates that the excitations
behave like fermions, two of which cannot occupy the same pigment. The second term $H_{ph}$ is the Hamiltonian of the environmental phonons, where the $\xi$th mode is described by the dimensionless coordinate, $q_\xi$. The last term $H_{el-ph}$ describes the coupling of the phonons to the electronic excitations,

$$H_{el-ph} = \sum_m B_m^\dagger B_m u_m,$$

where $u_m = -\sum_\xi c_{m\xi} q_\xi$, with $c_{m\xi}$ being the coupling constant between the $m$th pigment and the $\xi$th phonon mode. The quantity $u_m$ is the so-called collective energy gap coordinate [24] describing fluctuations in electronic energy and dissipation of reorganization energy. In this paper, we assume that fluctuations in electronic energies of different chlorophylls are not correlated, unless otherwise noted.

For the model expressed in equations (1)–(3), the present authors have presented a reliable theoretical framework to describe EET in PPCs specifically addressing site-dependent reorganization of protein environments [26]–[28], which play a significant role in the EET. The framework reduces to the conventional Redfield and Förster theories in their respective limits of validity [27]. This capability of interpolating between the two is crucial in order for the framework to be reliable in describing photosynthetic EET, which can occur between these two regimes. In the theory, the environmental effects at a finite temperature enter as follows: owing to the Gaussian property of the phonons, the environmental effects can be characterized fully by two two-point correlation functions of the collective energy gap coordinate $u_m$, i.e. the symmetric correlation function and the response function,

$$S_m(t) = \frac{1}{2}\langle[\tilde{u}_m(t), \tilde{u}_m(0)]\rangle_{ph},$$

$$\chi_m(t) = \frac{i}{\hbar}\langle[\tilde{u}_m(t), \tilde{u}_m(0)]\rangle_{ph},$$

respectively, where a tilde indicates an operator in the interaction picture. When the protein environment can be described classically, the two functions satisfy the classical fluctuation–dissipation theorem [29]:

$$\frac{d}{dt}S_m(t) \simeq -k_B T \chi_m(t),$$

with $k_B$ and $T$ being the Boltzmann constant and temperature, respectively. This theorem guarantees that thermal equilibrium is reached at long times. All the calculations of quantum dynamics in this paper are performed with the theory. When the classical approximation breaks down, quantum correction terms [28, 30] are included in the calculations.

For numerical calculations of EET processes in LHCII, we employ the Franck–Condon energies given in [19]. At present, no direct and detailed information is available on the symmetrized correlation functions and the response functions for LHCII. Hence, we employ the overdamped Brownian oscillator model [24] with the assumption that the functions for the individual chlorophylls are equivalent, $S_m(t) \equiv S(t)$ and $\chi_m(t) \equiv \chi(t)$. We adopt $\lambda = 35$ cm$^{-1}$ and $\tau_{\text{rexp}} = 50$ fs as the values of reorganization energy and relaxation time of the phonons associated with the individual chlorophyll, respectively, which were employed in numerical fitting of two-dimensional electronic spectra of the Fenna–Matthew–Olson (FMO) complex isolated from green sulfur bacteria [31].
3. Quantum entanglement in LHCII

The problem of measuring quantum entanglement is an active field of research of its own [32]. Extensive efforts have been made and numerous formulations have been proposed for the quantification of the entanglement. In order to explore the entanglement in LHCII, we employ the logarithmic negativity [32, 33] that quantifies the entanglement across a bipartition \((A|B)\) of a composite system and is defined by

\[
E(A|B) = \log_2(2N_{AB} + 1).
\]  

In the above, \(N_{AB}\) is the so-called negativity [32, 34, 35] expressed as the absolute values of the sum of the negative eigenvalues of \(\rho^{T_A}\), where \(\rho\) is the reduced density operator and \(T_A\) denotes the partial transposition with respect to subsystem \(A\).

Here, we discuss time evolution of the quantum entanglement in LHCII quantified by the logarithmic negativity. Because the intensity of sunlight is weak, simultaneous excitation of multiple chlorophylls can be assumed to be almost impossible under physiological situations. Therefore, we consider excitation of a single chlorophyll as an initial condition of the calculations. Figure 2 presents the entanglement dynamics for different bipartitions and initial excitations at the physiological temperature of 300 K. In figure 2(a), the bipartition is \(A = \{\text{Chla}612\}\) and \(B = \{\text{all the other Chls}\}\), and the initially excited pigment is Chla612. On the other hand, figure 2(b) shows the entanglement dynamics for the bipartition of \(A = \{\text{all the Chlas}\}\) and \(B = \{\text{all the Chlbs}\}\) with the initial excitation of Chlb606. Both plots in figure 2 show finite values in the long time region, as opposed to a decay to zero as has been previously reported [11]. This nonvanishing entanglement was also predicted theoretically in the FMO complex [10]. In order to clarify the issue, we again consider the PPC Hamiltonian given...
in equations (1) and (2). Because neither nonadiabatic transitions nor radiative/nonradiative decays from $|\varphi_{me}\rangle$ to $|\varphi_{mg}\rangle$ are assumed, the number of initial elementary excitations is conserved and thus the PPC Hamiltonian can be expressed by the direct sum as

$$H_{PPC} = H_{PPC}^{(0)} \oplus H_{PPC}^{(1)} \oplus \cdots,$$

where $H_{PPC}^{(n)}$ ($n = 0, 1, \ldots$) describes an $n$-exciton manifold comprising $n$ elementary excitations. Correspondingly, the electronic Hamiltonian can be decomposed as $H_{el} = H_{el}^{(0)} \oplus H_{el}^{(1)} \oplus \cdots$. Therefore, figure 2 can be discussed only in terms of the single-exciton manifold $H_{el}^{(1)}$, where the presence of a single excitation localized on the $m$th chlorophyll is expressed as $|m\rangle \equiv |\varphi_{me}\rangle \prod_{k \neq m} |\varphi_{kg}\rangle$. Within this manifold, equation (7) can be expressed as [12]

$$\mathcal{E}(A|B) = \log_2 \left( 1 + 2 \sqrt{\sum_{m \in A} \sum_{n \in B} |\langle m|\rho|n\rangle|^2} \right),$$

which allows us to analyze the entanglement in more detail. Here, it should be noticed that $|m\rangle$ is not an eigenstate of the Hamiltonian because of the presence of the excitonic coupling $J_{mn}$. Therefore, off-diagonal elements of the density matrices in the $\{|m\rangle\}$ basis do not necessarily vanish, and thus it is not surprising that the logarithmic negativity shows finite values in the long time region, i.e. the presence of the robust quantum entanglement. Actually, the electronic Hamiltonian $H_{el}^{(1)}$ given in [19] produces the energy eigenstates involving Chla612 or Chlb606 as follows:

$$|e_1\rangle \simeq 0.58|a610\rangle + 0.46|a611\rangle - 0.66|a612\rangle,$$

$$|e_2\rangle \simeq 0.81|a610\rangle - 0.26|a611\rangle + 0.52|a612\rangle,$$

$$|e_3\rangle \simeq 0.26|a603\rangle + 0.81|a611\rangle + 0.51|a612\rangle,$$

$$|e_5\rangle \simeq 0.96|a604\rangle - 0.24|b606\rangle,$$

$$|e_8\rangle \simeq 0.23|a604\rangle + 0.84|b606\rangle - 0.38|b608\rangle - 0.23|b609\rangle,$$

where $|e_\mu\rangle$ is the $\mu$th eigenstate of $H_{el}^{(1)}$ and the label $\mu$ gives the rank starting with the smallest eigenenergy. After the environment-induced noise destroys the quantum coherence between the eigenstates (or correspondingly the wave-like motion of an electronic excitation), the electronic states converge to the above eigenstates in equilibrium. Following the definition of quantum entanglement, these delocalized states are also entangled states because the eigenstates can be expressed in the form

$$|e_\mu\rangle = C_{\mu1}|\varphi_{1e}\rangle \prod_{n \neq 1} |\varphi_{ng}\rangle + C_{\mu2}|\varphi_{2e}\rangle \prod_{n \neq 2} |\varphi_{ng}\rangle + \cdots,$$

where $\{C_{\mu n}\}$ are coefficients for the superpositions. According to equation (9), the nonvanishing entanglement in figure 2(a) is caused by $|e_1\rangle$, $|e_2\rangle$ and $|e_3\rangle$, whereas those in figure 2(b) are caused by $|e_8\rangle$ and $|e_{13}\rangle$. In figure 2(b), the minimum in the logarithmic negativity arises from the energy relaxation from $|e_{13}\rangle$ to $|e_8\rangle$. This negativity is mainly dominated by $|\langle a604|\rho|b606\rangle|^2$. In the course of the energy relaxation, the real part of $\langle a604|\rho|b606\rangle$ changes from positive to negative values, as can be seen in coefficients of equations (13) and (14). As a result, its absolute square $|\langle a604|\rho|b606\rangle|^2$ and thus the logarithmic negativity exhibit a local minimum.
Therefore, the behavior in figure 2(b) can be interpreted as destruction and construction of energy eigenstates accompanied by the energy relaxation from $|e_{13}\rangle$ to $|e_8\rangle$.

From the standpoint of physical chemistry, these quantum delocalized states or quantum entangled states in complex molecular systems are ubiquitous and experimentally detectable [24, 25, 36]. Temperature-independent theories, such as the simple Lindblad equation that is extensively employed in the field of quantum information science or quantum optics [8], are not capable of producing the nonvanishing quantum entanglement in equilibrium shown in figure 2. However, the vanishing entanglement in the PPCs is an erroneous conclusion caused by an oversimplified treatment of the environment-induced fluctuation–dissipation processes.

4. Discussion

Although the quantum entanglement in the single-exciton manifold is conceptually the same as the quantum delocalization caused by the excitonic coupling, investigations with tools quantifying the entanglement provide us with some insights into quantum delocalized states found in photosynthetic EET problems. Here, we discuss the eigenstate representation of the electronic Hamiltonian describing $N$ pigments within the single-exciton manifold,

$$H_{el}^{(1)}|e_\mu\rangle = E_\mu|e_\mu\rangle,$$

where $E_\mu$ is the $\mu$th eigenenergy of $H_{el}^{(1)}$ and $|e_\mu\rangle$ is the accompanying eigenstate expressed in equation (15). In the literature, these eigenstates are usually termed ‘excitons’. In addition, as a measure of how many molecules are involved in a given exciton, the inverse participation ratio (IPR) is employed. The IPR of the $\mu$th exciton is defined as [37, 38]

$$IPR_\mu = \frac{1}{\sum_{m=1}^{N} C_{\mu m}^4}.$$ 

If the eigenstate $|e_\mu\rangle$ is fully delocalized with $C_{\mu m} = 1/\sqrt{N}$, then the ratio becomes $IPR_\mu = N$. On the other hand, in the limit of complete localization such as $|e_\mu\rangle = |\phi_{m}\rangle \prod_{k \neq m} |\phi_k\rangle$, we have $IPR_\mu = 1$. Here, one should not overlook that these eigenenergies and coefficients are obtained via diagonalization of the electronic Hamiltonian in equation (2) comprising the Franck–Condon transition energies $h\Omega_m$ and the excitonic couplings $hJ_{mn}$. These are independent of any information on the environment such as temperature and reorganization energy. However, the energies and coefficients of the actual excitons will deviate from the values of $E_\mu$ and $C_{\mu m}$ because of the environment-induced fluctuation–dissipation processes. Therefore, it is reasonable to think that dynamic interaction with the electronic states and the environment will change the nature of the delocalized states expressed in equation (15).

4.1. Characterization of quantum delocalized states affected by the environment

In order to clarify this issue, we consider a coupled homo-dimer consisting of the four states, $|0\rangle = |\phi_{1g}\rangle|\phi_{2g}\rangle$, $|1\rangle = |\phi_{1e}\rangle|\phi_{2g}\rangle$, $|2\rangle = |\phi_{1g}\rangle|\phi_{2e}\rangle$ and $|1, 2\rangle = |\phi_{1e}\rangle|\phi_{2e}\rangle$, coupled to the phonon environment. Then, the electronic and electron–phonon coupling Hamiltonians in equations (2) and (3) is represented as

$$H_{el} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & h\Omega & hJ & 0 \\ 0 & hJ & h\Omega & 0 \\ 0 & 0 & 0 & 2h\Omega \end{pmatrix}, \quad H_{el-ph} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_1 + u_2 \end{pmatrix}.$$ 


respectively, which yield the ‘excitons’ in the single-exciton manifold as \( |e_{\pm} \rangle = (|1\rangle \pm |2\rangle) / \sqrt{2} \), and an IPR of \( IPR_{\pm} = 2 \), irrespective of the electron–phonon coupling parameters. On the other hand, we can adopt Wootters’ concurrence to quantify the quantum entanglement in the dimer (two qubits) [39, 40]. If the reduced density operator has the so-called X structure [41],

\[
\rho = \begin{pmatrix}
    a & 0 & 0 & w \\
    0 & b & z & 0 \\
    0 & z^* & c & 0 \\
    w^* & 0 & 0 & d
\end{pmatrix},
\]

then the concurrence can be expressed as

\[
C = 2 \max \left\{ 0, |z| - \sqrt{ad}, |w| - \sqrt{bc} \right\}.
\]

Therefore, the quantum entanglement in the single-exciton manifold is quantified simply by

\[
C = 2 |\langle 1 | \rho | 2 \rangle|.
\]

For calculations of the concurrence, we employ again the overdamped Brownian oscillator model [24] with the assumption that the symmetrized correlation and response functions associated with the individual pigments are the same for each site. In figure 3, we present the calculated concurrence in thermal equilibrium for various parameters. Unless otherwise noted, we employ \( J = 100 \text{ cm}^{-1}, \lambda = 50 \text{ cm}^{-1}, T = 300 \text{ K} \) and \( \tau \times n = 100 \text{ fs} \) as the default values of the excitonic coupling, reorganization energy, temperature and phonon relaxation time, respectively [27]. We have chosen these values because they are typical for photosynthetic EET [42]. Figure 3(a) shows the concurrence as a function of the excitonic coupling strength, \( J \). Unlike the IPR of the homo-dimer, the concurrence increases with increasing excitonic coupling. This result is reasonable because the excitonic coupling \( J \) is the transition rate and a faster transition rate resulting from a larger \( J \) will construct more robust quantum delocalization or correspondingly more robust quantum entanglement. More interesting results are seen in figures 3(b) and (c). Figure 3(b) shows the concurrence as a function of reorganization energy \( \lambda \), whereas figure 3(c) shows the concurrence as a function of temperature \( T \). Figures 3(b) and (c) demonstrate that the concurrence decreases with increasing reorganization energy and temperature. These tendencies can be explained as follows. The fluctuation–dissipation theorem in equation (6) allows us to express the root-mean-square amplitude of fluctuations in the electronic energy of the \( m \)th pigment as \( \Delta \Delta_m \simeq \sqrt{2 \hbar \lambda k_B T} \) [24]. In addition, a larger reorganization energy gives rise to a higher energetic barrier separating the excitation located on individual chlorophylls, as was discussed in figure 5 of [27]. Therefore, larger reorganization energy and higher temperature cause a kind of localization called dynamic localization [36, 43]. The reorganization energy dependence in figure 3(b) and the temperature dependence in figure 3(c) indicate the dynamic localization, whereas traditional discussions of quantum delocalization such as the IPR do not capture the localization. Finally, figure 3(d) presents the concurrence as a function of a phonon relaxation time, \( \tau \times n \). The concurrence in figure 3(d) is not sensitive to the relaxation time because our discussion here is focused on the steady-state entanglement in the thermal equilibrium after time-dependent transient events. We note, however, that the relaxation time plays a significant role in protecting long-lasting quantum wave-like motion [27, 28] and entanglement dynamics [9, 44]. As demonstrated in [23, 27], sluggish dissipation of reorganization energy increases the time that an electronic excitation stays above an energetic barrier separating pigments. As a result, the slower timescale of the
Figure 3. Quantum entanglement in the single-exciton manifold of a homodimer in thermal equilibrium, as a function of (a) excitonic coupling $J$, (b) reorganization energy $\lambda$, (c) temperature $T$ and (d) phonon relaxation time $\tau r\times n$. We employ $J = 100\,\text{cm}^{-1}$, $\lambda = 50\,\text{cm}^{-1}$, $T = 300\,\text{K}$ and $\tau r\times n = 100\,\text{fs}$ as the default values.

phonon relaxation prolongs delocalization over the multiple pigments and hence the long-lived wave-like motion is sustained. However, the entanglement shown in figure 3 is obtained after the destruction of this wave-like motion.

4.2. Impact of correlated fluctuations in electronic energies of different pigments

So far we have discussed the quantum entanglement or superposition under the assumption that fluctuations in electronic energies of different pigments are not correlated. In the remaining part
of this section, we discuss the influence of correlated fluctuations in the pigment electronic energies. Recently, Lee et al [4] clearly demonstrated that strongly correlated fluctuations between two sites preserve quantum coherence in a bacterial reaction center by applying a two-color electronic coherent photon echo technique. If different pigments experience the same dynamic effects from the same portion of the protein, fluctuations in their electronic energies would be correlated [45, 46]. To model the correlated fluctuations, we consider the following Hamiltonian instead of equation (3):

\[
H_{el-ph} = \sum_m B_m^\dagger B_m \left[ x_{mm} u_m + \sum_{k(\neq m)} x_{mk} u_k \right],
\]

with \( x_{mk} \) being real coefficients, where fluctuations in the electronic energy of the \( m \)th pigments can be described by

\[
U_m = \sum_k x_{mk} u_k.
\]

Thus, the auto-correlation function of \( U_m \) is obtained as

\[
\langle \tilde{U}_m(t) \tilde{U}_m(0) \rangle_{ph} = \sum_k x_{mk}^2 \langle \tilde{u}_k(t) \tilde{u}_k(0) \rangle_{ph},
\]

while the cross-correlation function \((m \neq n)\) is

\[
\langle \tilde{U}_m(t) \tilde{U}_n(0) \rangle_{ph} = \sum_k x_{mk} x_{nk} \langle \tilde{u}_k(t) \tilde{u}_k(0) \rangle_{ph}.
\]

It is important to note that this cross-correlation function can be positive or negative, as discussed in the context of two-dimensional infrared spectroscopy [47, 48]. For calculations for the homo-dimer, we address a simple case for the coefficients \( \{x_{mn}\} \),

\[
\left( \begin{array}{cc} x_{11} & x_{12} \\ x_{21} & x_{22} \end{array} \right) = \frac{1}{\sqrt{1 + \zeta^2}} \left( \begin{array}{cc} 1 & \zeta \\ \zeta & 1 \end{array} \right) \quad (-1 \leq \zeta \leq 1),
\]

which yields the auto- and cross-correlation functions as

\[
\langle \tilde{U}_1(t) \tilde{U}_1(0) \rangle_{ph} = \langle \tilde{U}_2(t) \tilde{U}_2(0) \rangle_{ph} = S(t) - \frac{i \hbar}{2} \chi(t),
\]

\[
\langle \tilde{U}_1(t) \tilde{U}_2(0) \rangle_{ph} = \langle \tilde{U}_2(t) \tilde{U}_1(0) \rangle_{ph} = \alpha \left[ S(t) - \frac{i \hbar}{2} \chi(t) \right],
\]

with the cross-correlation coefficient, \( \alpha (-1 \leq \alpha \leq 1) \), defined by

\[
\alpha = \frac{2\zeta}{1 + \zeta^2} \quad (-1 \leq \zeta \leq 1).
\]

In figure 4, we present the influence of the correlated fluctuations upon (a) the EET dynamics and (b) the steady-state concurrence in the homo-dimer for various values of the cross-correlation coefficient, \( \alpha \). The other parameters are chosen to be \( J = 100 \text{ cm}^{-1}, \lambda = 500 \text{ cm}^{-1}, \tau_{\text{e-x}} = 100 \text{ fs} \) and \( T = 300 \text{ K} [27] \). Figure 4(b) clearly demonstrates that the positive correlation \((\alpha = +0.9, \text{ green line})\) enhances quantum coherent wave-like behavior in the EET dynamics, although the overall dynamics under uncorrelated fluctuations \((\alpha = 0, \text{ red line})\) is dominated by slow incoherent hopping. It is important to note that the initial fast decay of the uncorrelated
Figure 4. Impact of the correlated fluctuations in a homo-dimer upon (a) the electronic energy transfer dynamics and (b) the quantum entanglement in thermal equilibrium within the single-exciton manifold. We employ $J = 100 \text{ cm}^{-1}$, $\lambda = 500 \text{ cm}^{-1}$, $T = 300 \text{ K}$ and $\tau_{r \times n} = 100 \text{ fs}$.

case arises from quantum coherence despite the fact that the EET is in the Förster regime characterized by $\lambda > J$ [27]. On the other hand, the negative correlation ($\alpha = -0.9$, blue line) suppresses the incoherent hopping rate of the EET in comparison with the uncorrelated case. These behaviors can be understood in relation to the steady-state entanglement as a measure of quantum delocalization under the impact of the surrounding environment. Figure 4(b) demonstrates that the concurrence increases with increasing cross-correlation coefficient, $\alpha$. This is because positive correlation ($\alpha > 0$) decreases the height of the energy barrier separating the pigments [23] and thus increases the extent of the delocalization. As a result, quantum coherent wave-like motion can be observed in the EET dynamics. On the other hand, negative correlation ($\alpha < 0$) increases the height of the barrier [23]; therefore, the dynamic localization is enhanced and the concurrence decreases. In this case, the incoherent hopping motion becomes slower because the EET must overcome a higher energy barrier between the donor and the acceptor.

5. Summary

In this paper, we explored quantum entanglement in the most abundant photosynthetic light harvesting PPC, LHCII. The entanglement in the single-exciton manifold of LHCII is conceptually the same as the quantum delocalization of the exciton states caused by the excitonic coupling, and thus the presence of robust quantum entanglement in photosynthetic complexes is not unexpected. However, quantities characterizing the entanglement such as the logarithmic negativity and the concurrence provide us with more detailed information regarding the interplay between the quantum delocalization and the surrounding environment, specifically the dynamic localization and correlated fluctuation effects that are difficult for a traditional treatment such as the IPR to capture. Yet, it is not clear whether quantum mechanics or quantum information processing play significant and nontrivial roles in biological organisms. However,
the present work is encouraging in the sense that the concepts and tools developed in the field of quantum information science complement traditional views and broaden our horizons of the possible range of applications of quantum superpositions in biological systems.

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