Measures and implications of electronic coherence in photosynthetic light-harvesting

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We review various methods for measuring delocalization in light-harvesting complexes. Direct relations between inverse participation ratios (IPRs) and entanglement measures are derived. The B850 ring from the LH2 complex in *Rhodopseudomonas acidophila* is studied. By analysing electronic energy transfer dynamics in the B850 ring using different metrics for quantifying excitonic delocalization, we conclude that measures of entanglement are far more robust (in terms of time scale, temperature and level of decoherence) than IPRs, and are therefore more appropriate for the purpose of studying the time evolution of coherence in a system.

Keywords: B850; electronic coherence; delocalization; electronic energy transfer; entanglement; photosynthesis

1. Introduction

The first steps involved in solar energy conversion by photosynthesis are to capture the Sun’s energy and use it to promote charge separation in reaction centres (RCs). More prolific than RCs are the associated light-harvesting proteins. Light-harvesting proteins bind a high concentration of light-absorbing pigments. Their role is to absorb solar radiation, store that energy transiently as electronic excited states and transfer those electronic excitations to RCs. The diversity of light-harvesting protein structures has inspired studies of energy transfer that in turn have revealed various mechanisms at play [1–5].

A long-standing question has concerned the interplay of Förster-type energy transfer (from molecule to molecule) and coherent delocalization of electronic eigenstates (molecular excitons) [4]. The 1995 report from McDermott *et al.* [6] of the crystal structure of the peripheral light-harvesting complex LH2 from the purple anoxygenic bacterium *Rhodopseudomonas (Rps.) acidophila* strain 10050 initiated detailed studies of exciton delocalization. At this time, researchers were

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interested in how many bacteriochlorophyll-a (Bchl-a) molecules in the B850 ring of LH2 were involved in photoexcitation, dynamics of energy transfer and fluorescence. Thus, a ‘delocalization length’ was hotly debated [7].

Recent studies of photosynthetic proteins, including the Fenna–Matthews–Olson (FMO) complex from green sulfur bacteria [8,9], the major light-harvesting complex from higher plants and green algae (LHC-II) [10,11], and the major light-harvesting complex from cryptophyte algae (PE545 and PC645) [12], have been undertaken using two-dimensional electronic spectroscopy. It has been discovered that even rather subtle excitonic effects are quite robust against decoherence—even at physiological temperatures [12]. The ability to follow the evolution of quantum coherence with time in these experiments means that it is desirable to quantify not only a delocalization length, but how delocalized electronic states decohere and localize—and to elucidate the underlying causes. For such purposes, measures have been developed in quantum information science [13,14]. Those measures have recently been applied to examine the evolution of delocalization during energy transfer dynamics in photosynthetic proteins [13,15–18].

While quantum information measures can allow for bold claims such as the presence of entanglement in biological systems [15], their real advantage is that such measures come readily equipped to examine the properties of quantum coherence: from how it is distributed [19], to how it is limited by decoherence [20]. Therefore, it is worth comparing standard delocalization measures such as the inverse participation ratio (IPR) [21,22] with these more recent measures, in an effort to understand the relations between them and to ascertain which ones are of merit. In this present work, we employ the B850 ring as a model to explore the connections between various delocalization measures, and through the use of static and dynamic models, expose their strengths and weaknesses. Our results demonstrate that entanglement measures, such as the total tangle [17], provide a far more accurate picture of the delocalized nature of photosynthetic excitation than that which other measures, such as the IPR, can provide.

2. Electronic coherence in energy transfer

Photosynthetic systems are prime examples of nature exploiting electronic coherence. Individual chromophores collectively absorb and distribute energy; if electronic couplings between the chromophores are large enough compared with line broadening, then the excitation can be coherently shared among chromophores [23,24]. These collective excitations, known as excitons, provide a means of producing ‘new’ chromophores from the existing molecular building blocks. These new chromophores take over the roles of donors and acceptors for energy transfer, and can have a profound influence on energy transfer rates compared with a similar system where energy flows through localized states; rather than the excitation hopping incoherently from site to site, the system can coherently control the dynamics of energy migration so that the excitation travels in a wavelike manner, through interference of multiple pathways [3,25,26]. Even when electronic coupling is quite small, for example in PC645 and PE545, quantum coherence ‘wires’ together the chromophores across the unit [12].
The LH2 light-harvesting complex of Rps. acidophila serves as a useful model for contrasting the two regimes of electronic energy transfer (EET): localized and collective excitations. The LH2 pigment–protein complex, which we describe in detail in §4, is composed of two spectrally distinct molecular rings: the B800 and the B850, so-called owing to the wavelength (in nanometres) at which they most strongly absorb. In both cases, Bchl- \( \text{a} \) acts as the molecular chromophore. However, the chromophores within B800 are so weakly coupled (approx. 30 cm\(^{-1}\)) that the excitation is mainly localized on a single site, though there is still some coherence [27]. By contrast, the B850 chromophores are strongly coupled (approx. 300 cm\(^{-1}\)), leading to strong delocalization of electronic excitation.

A common assumption made with bacterial light-harvesting complexes is that there is at most one excitation in the system. This is a reasonable approximation given the typical sunlight irradiance [28], as well as the fine interplay between light intensity and the ratio of the number of light-harvesting complexes to RCs [29,30]. As a first approximation, the B850 ring can be modelled as a perfectly symmetric ring of \( N = 18 \) coupled, two-level systems, with equal site energy \( E_{\text{Bchl}} \) and nearest-neighbour coupling \( U \), where the electronic Hamiltonian is given by

\[
H_e = \sum_{n=1}^{N} E_{\text{Bchl}} |n\rangle\langle n| + \sum_{n=1}^{N} U(|n\rangle\langle n+1| + \text{h.c.}), \tag{2.1}
\]

where \( |n\rangle \) denotes the state with the excitation localized on chromophore \( n \) and \( |N+1\rangle \equiv |1\rangle \). The excitons for this system are simply the eigenstates \( \Phi_k \) of equation (2.1), where the excitonic energies are given by \( E_k = E_{\text{Bchl}} - 2U \cos(2\pi k/N) \) with \( k = 0, -1, 1, -2, 2, \ldots, -8, 8, 9 \). It is the electronic coupling that gives rise to a manifold of delocalized excited states; in the absence of such couplings, the Hamiltonian in equation (2.1) would already be in diagonal form and the site basis would correspond to the eigenstates of the system. To exemplify this point, we examine the absorption spectrum of a subunit of the LH2, consisting of three Bchl- \( \text{a} \) molecules (a dimer of B850 chromophores with one B800 chromophore), without (figure 1a) and with (figure 1b) inter-site coupling. The inter-site coupling causes a shift in eigenenergies, expanding the absorption spectrum. The increased amplitude at 840 nm comes from the change to the transition strength, as the individual dipole transition moments form exciton dipole moments.

Under zero disorder, the only non-degenerate eigenstates in the B850 ring are the upper \( (k = 9) \) and lower \( (k = 0) \) states; the remaining states \( (k = -1, 1, \ldots, -8, 8) \) are twofold degenerate. Using the above approximation, it is simple to show that the top and bottom excitons are delocalized over the entire ring, while the remaining degenerate states have a delocalization ranging (through superposition of degenerate eigenstates) from two-thirds of the ring to the entire ring. However, given that the B850 ring presents a dimeric structure, such that the inter-dimer and intra-dimer electronic couplings have different values, the reality is that there is a range of delocalization lengths. This range is extended further by the presence of inhomogeneous and homogeneous broadening, which we discuss in §4. Delocalization has a significant impact on EET in photosynthetic systems. In particular, it has been shown that the presence of strong electronic coherence accelerates energy transfer from the B800 to the B850 ring [3,26].
Figure 1. Simulated absorption spectrum for the LH2 subunit (containing one B850 dimer, and one B800 monomer), with (a) no coupling and (b) coupling. The vertical lines correspond to the site transition energies and exciton transition energies, respectively; the B800 monomer contribution is represented by the dashed line. (Online version in colour.)

The importance of delocalized excitations has therefore prompted researchers to quantify ‘delocalization length’, or coherence size, in molecular systems and photosynthetic light-harvesting antenna systems.

3. Quantum measures of electronic coherence

While many systems, such as the B850 ring, should in theory exhibit a delocalized character, some experimental evidence of this delocalization is required. Such evidence exists in the spectroscopic effect known as superradiance. In an exciton manifold, the exciton dipole strength can be significantly larger than that of a monomer. Because the dipole strength is directly related to the radiative rate, we can therefore observe exciton delocalization by an often marked increase in the radiative rate. This is especially evident in strongly coupled molecular aggregates,
such as J-aggregates. J-aggregates possess a strong narrow absorption band, red-shifted with respect to that of the monomer. This so-called J-band is due to the fact that the majority of the aggregate dipole strength is concentrated on the lowest-energy exciton transition \([31–33]\).

In the case of the B850 ring, this lowest transition is optically forbidden in the absence of heterogeneity in the system. This is because the transition dipoles of the B850 ring are arranged in a head-to-head, tail-to-tail manner, resulting in the concentration of the overall transition strength at the degenerate \(k = \pm 1\) states, which share it equally. Consequently, the most delocalized states \((k = 0, 9)\) are optically dark, as the \(k = \pm 1\) states may not be fully delocalized. However, this is the only case when there is no inhomogeneous broadening. In the presence of energetic disorder, which is mainly diagonal \([34]\), the degeneracy in the system is lifted and the oscillator strength is redistributed among the exciton states, increasing the transition strength of the \(k = 0\) state. As disorder increases, the site energies become increasingly varied, and in cases of extreme disorder, the ring adopts a monomeric form, setting the individual transition dipoles to 1. According to Monshouwer et al. \([35]\), superradiance is a useful measure of delocalization only in J-aggregates, where the dipole strength is concentrated on the lowest single-exciton level. As Dahlbom et al. \([36]\) note, the change in geometry and environment strongly affects the superradiant measurements; for a measurement yielding a value of \(L\), the delocalization length can be interpreted as \(L\) or \(N - L\), where \(N\) is the system size. Nevertheless, superradiance does provide a possible lower bound for the delocalization length of the B850 complex. As such, Monshouwer et al. \([35]\) recorded a delocalization size of 4 ± 2. Indeed, Pullerits et al. \([37]\) first reported this value in 1995, noting that the delocalization extends from one to three dimers in the B850 ring.

Book et al. \([38]\) arrived at a much larger delocalization size, approximately 13, using pump–probe measurements at zero delay. By noting that pump–probe signals scale to the fourth power of the transition dipole moment, and assuming that the B800 ring was monomeric, they compared the B850 and B800 signals in order to estimate the delocalization size of the B850 ring. This ratio can be expressed as

\[
\frac{S_{\text{B850}}}{S_{\text{B800}}} = \frac{(18/N_L)(N_L^{1/2}/\mu_{\text{BChl}})^4}{9\mu_{\text{BChl}}^4}.
\]

(3.1)

From this ratio, we obtain the delocalization length

\[
N_L = \frac{1}{2} \frac{S_{\text{B850}}}{S_{\text{B800}}}.
\]

(3.2)

Here, \(N_L\) is the delocalization length of the B850 ring, and \(\mu_{\text{BChl}}\) is the transition dipole moment of a single Bchl-\(a\) molecule. This value agreed with that found by Leupold et al. \([39]\), who estimated the delocalization size to be within the range of 12–18. However, both authors assume that the transition dipole of the exciton scales with \(N_L^{1/2}\), an assumption only valid in the case of superradiant J-aggregates. As efforts in the field to pinpoint the delocalization size of the B850 ring resulted in values ranging from one or two dimers (some reporting 4 ± 2 \([35,37,40]\) to the entire ring \([39,41–43]\), it was evident that delocalization was not a static value, and that it strongly depended on the type of experiment conducted and on the underlying theoretical assumptions. As noted by Book et al. \([38]\)
and Nagarajan et al. [44], the time scale of the experiment is a crucial factor in determining the delocalization length. For instance, in fluorescence emission studies, the measured value depends on the excited-state lifetime of the system, giving the exciton time to dephase and lose coherence, thus yielding small-sized values [35]. Experiments such as transient absorption, hole burning and circular dichroism yield much larger values [42,45], while pump–probe measurements have tuneable delay times, providing intermediate delocalization levels [38].

There are two main classes [46] of measures of delocalization in singly excited states: one deals with individual excitonic states, whereas the other involves exciton wavepackets (represented by density matrices), as either a coherent superposition or a statistical mixture of individual exciton states. The density matrix describing the state of a system includes the populations \( r_{nn} \) and the coherences \( r_{nm} \), and describes either pure or mixed states.

A pure state is known exactly, and can be written as \( \rho = |\psi\rangle \langle \psi| \), whereas a mixed state is a statistical mixture of several wave functions, each with some probability \( p_j \), \( \rho = \sum_{m,n} p_j |\psi_j\rangle \langle \psi_j| \). This means that the advantage of the latter type of delocalization measure, i.e. on exciton wavepackets, is that its value evolves with the system; the advantage of the former type is that for a pure state it requires \( N \) rather than \( N^2 \) measurements.

**a) Single-exciton measures**

The most frequently employed single-exciton delocalization measure is the IPR [21,46–50]. For a given exciton \( |\psi\rangle = \sum_n a_n|n\rangle \), the IPR is the sum of the fourth power of the site amplitudes, and can range from \( 1/N \) for a fully delocalized state to 1 for a fully localized state,

\[
\text{IPR} = \sum_{n=1}^{N} |a_n|^4.
\]

It should be noted that several versions of the IPR are defined, often erroneously, in the literature [51]. The earlier-mentioned measure shown, however, is the original definition by Thouless [21]; the participation ratio (PR) is the number of molecules participating in an exciton, and therefore the IPR is the reciprocal of that function. Often, the IPR is used to describe the PR and vice versa [46,49]; however, we will continue to use the historical (and more intuitive) definition. While the IPR is defined for pure states, for the purpose of comparison, we will express the IPR as a function of the exciton density matrix in the site basis, as a sum of the square of site populations,

\[
\text{IPR}(\rho) = \sum_{n=1}^{N} \rho_{nn}^2.
\]

Slightly modified versions of the IPR exist: Fidder et al. [48] employed an IPR measure as a function of exciton energy, weighted by the inverse of \( D(\varepsilon) \), the density of states, for an ensemble average of a randomly generated aggregate of states,

\[
L(\varepsilon) = \frac{1}{N} \frac{\langle \sum_k \Delta(\varepsilon - \varepsilon_k)(\sum_{n=1}^{N} a_{kn}^4) \rangle}{D(\varepsilon)},
\]

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where $\Delta(\varepsilon - \varepsilon_k) = 1/R$ for $|\varepsilon - \varepsilon_k| \leq R/2$ and $\Delta(\varepsilon - \varepsilon_k) = 0$ otherwise. $R$ is the resolution of the spectrum, so that $\Delta$ acts as a delta function for eigenenergy $\varepsilon_k$.

Leegwater [52] developed a version of delocalization length ($R^{-1}$) that he described as the time-integrated probability that an excitation remained at a particular site, weighted by the dephasing time $\Gamma^{-1}$,

$$R = \frac{1}{N} \sum_{i,k,k'} |\langle i| \psi_k \rangle|^2 \frac{\Gamma^2}{\Gamma^2 + (\varepsilon_k - \varepsilon_{k'})^2} |\langle i| \psi'_{k'} \rangle|^2,$$

(3.6)

where $|\psi_k \rangle$ and $|\psi'_{k'} \rangle$ are eigenstates of the system. Under the limit of zero dephasing, this function becomes the average of the IPR (equation (3.3)) of all eigenstates.

Finally, wave function measures based on autocorrelation functions have also been developed [39]; we detail an enhanced version of this measure [53] in §3b.

All of the earlier-mentioned measures have the common limitation that they are defined for single excitons, and therefore are not well suited to study the time evolution of excitation localization in systems that are evolving under the effect of decoherence, where such states become mixed.

(b) Exciton wavepacket measures

In general, IPR measures only take into account the diagonal values of a density matrix, and ignore the coherences. This limitation has been addressed by Kühn & Sundström [53], and by Mukamel [22,36,54,55]. Kühn & Sundström sought to plot a distribution of the inter-site coherences, based on the separation between the sites:

$$C_n(t) \equiv \sum_{m} |\langle r_{mn}(t) \rangle_{\text{disorder}}|^2.$$

(3.7)

In the case of the B850 ring, the value $n$ runs from 0 to 8, halfway across the B850 ring. $C_0$ gives the total exciton population, $C_1$ gives the total nearest-neighbour coherences, $C_2$ gives the total next-nearest-neighbour coherences and so on.

The delocalization length was then estimated by measuring the full width at half-maximum (FWHM) of $C_n$ at any given point in time. However, this may not be a very accurate nor practicable technique; the $C_n$ functions can exhibit oscillatory behaviour, and, as such, calculating the FWHM of these functions is not feasible.

Mukamel and co-workers took a simpler approach with what they termed the IPR of the exciton density matrix [22]. For clarity, we will refer to it as the coherence length (CL):

$$\text{CL}(t) \equiv \frac{\left(\sum_{m,n} |\rho_{mn}(t)|\right)^2}{N \sum_{m,n} |\rho_{mn}(t)|^2}.$$

(3.8)

Unlike the original IPR (equation (3.3)), the CL (equation (3.8)) takes into account the magnitudes of the off-diagonal elements of the density matrix; the more correlated the sites are, the larger the CL. The CL ranges from 1 for a state with zero coherence to a value of $N$ for a fully delocalized state. As its popularity within the field would suggest [36,38,46,55–58], the CL appears as a
much more effective measure of delocalization; still, the CL is not without its issues, which we will address after discussing the concept of entanglement, and how its quantification can serve as a tool to measure exciton delocalization.

(c) Entanglement and coherence

Quantum effects such as entanglement and coherence are normally treated as separate phenomena; entanglement describes correlations that exceed those allowed by classical physics, whereas coherence is commonly associated with interference effects. In the single-excitation manifold, the two effects conveniently become mathematically equivalent.

An entangled state is one that cannot be written as a product state, as it is not separable. For pure states, one writes this condition in terms of wave functions, \(|\psi\rangle \neq |\psi_1\rangle \otimes |\psi_2\rangle \otimes \cdots \otimes |\psi_n\rangle\). Mixed states, however, are entangled if they cannot be written as a convex combination of product states, \(\rho \neq \sum_i p_i |\rho_i\rangle \otimes \cdots \otimes |\rho_n\rangle\), where \(0 < p_i < 1\), and \(\sum p_i = 1\). Quantum coherence is manifested as the presence of off-diagonal elements in the density matrix. In the single-excitation manifold, the presence of entanglement implies coherence and vice versa [15]; in other words, coherence is not only a necessary but also a sufficient condition for the existence of entanglement. Therefore, any measure of entanglement is also a measure of quantum coherence. In general, quantifying entanglement for mixed states is a difficult task, and many different measures have been proposed. For a review, see Plenio & Virmani [13] and Horodecki et al. [14]. One such measure is the entanglement of formation, which for a pair of two-level systems can be directly related to a quantity known as the concurrence [59]. When we are restricted to the single-exciton subspace, the concurrence takes the simple form

\[ C_{mn}(t) = 2|\rho_{mn}(t)|, \]  

from which the direct relation between coherence and entanglement is evident.

An interesting feature of multipartite entanglement is that entangled states are monogamous; that is, for any system with \(N\) two-level sites, whether pure or mixed [60], there is a restriction on how quantum correlations are distributed. A commonly used example is as follows: Given three particles, if two are maximally entangled, then the third can be in no way entangled with either of the other two. If two particles are partially entangled, then there is a limit to how entangled either particle is with a third. As first demonstrated by Coffman et al. [19], for pure states of three two-level systems, and later generalized by Osborne & Verstraete [60], for mixed states and an arbitrary number of two-level systems, the square of the concurrence, the tangle \(\tau_{mn}(t) = 4|\rho_{mn}(t)|^2\), is bounded by the monogamy of entanglement in the following way:

\[ \sum_{m=1, n\neq m}^N \tau_{mn} \leq \tau_n, \]  

where \(\tau_n\) is the tangle between the partition of site \(n\) and the rest of the system. For pure states, \(\tau_n\) is given by \(4\det \rho_n\), where \(\rho_n\) denotes the reduced density matrix of the \(n\)th site [59,60]. In analysing measures that seek to quantify the coherence of light-harvesting complexes (LHCs), it is worth investigating whether monogamy of entanglement has any role to play in the energy transfer process.
In this direction, Fassioli & Olaya-Castro [17,18] have analysed the distribution of entanglement in the FMO complex and its implications on the quantum yield (the probability that an absorbed photon is trapped in the RC). For instance, they showed that entanglement between donor molecules correlates inversely with energy transfer efficiency.

\[(d) \text{Entanglement and participation ratios}\]

An advantage of the tangle measure is that it can be shown that the summation over all tangles $E_T(\rho)$ is related to the difference between the state’s purity and its IPR:

$$E_T(\rho) = 4 \sum_{m,n>m}^N |\rho_{mn}|^2 = 2[\text{Tr}(\rho^2) - \text{IPR}(\rho)]. \quad (3.11)$$

The purity of a density matrix, $\text{Purity}(\rho) = \text{Tr}(\rho^2)$, is a measure of how well known a state is. Its values range from $1/N$ (for a fully mixed state) to 1 (for a pure state).

The sum of the tangles between the $n$th site and the rest of the system provides an upper bound for the total tangle in equation (3.11),

$$E_T(\rho) \leq \frac{1}{2} \sum_{n=1}^N \tau_n. \quad (3.12)$$

In the case of pure states, and using $\tau_n = 4 \det \rho_n = 4 \rho_{nn}(1 - \rho_{nn})$, inequality (3.12) saturates, i.e.

$$E_T(t) = 2[1 - \text{IPR}(\rho)] = \frac{1}{2} \sum_{n=1}^N \tau_n. \quad (3.13)$$

Physically, this means that when the IPR is large (i.e. the excitation is fairly localized), the level of entanglement is low, showing again the equivalence between the presence of coherence (exciton delocalization) in a system and its entanglement.

We also get similar results for other entanglement measures [15,61,62].

For example, the same relation (up to a factor) was derived by Scholak et al. [62], in a paper that quantifies the $n$-party entanglement of a pure state:

$$E_2 = \sqrt{\frac{1}{1 - 1/N}(1 - \text{IPR}(\rho))}. \quad (3.14)$$

Another measure of multipartite entanglement, employed by Sarovar et al. [15], quantifies global entanglement based on the relative entropy and is given by

$$E(\rho) = -\sum_{n}^N \rho_{nn} \ln \rho_{nn} - S(\rho). \quad (3.15)$$

This measure compares the Von Neumann entropy $S(\rho) = -\text{Tr}(\rho \ln \rho)$ of the state with its closest separable state, where the latter is given by the diagonal of the state’s density matrix.
In the case of a pure state, the Von Neumann entropy is zero, and the global entanglement equation (3.15) simply reduces to the Von Neumann entropy of its closest separable state. For such a separable state, the Von Neumann entropy is equivalent to the Shannon entropy. As such, the IPR and Shannon entropy are proportional to different orders ($\alpha$) of the Rényi entropy,

$$H_{\alpha}(\rho) = \frac{1}{1 - \alpha} \ln \left( \sum_n \rho_{nn}^\alpha \right),$$  \hspace{1cm} (3.16)

with $\alpha = 2$ being inversely proportional to the IPR, and $\alpha = 1$ being equal to the Shannon entropy.

Under decoherence, the direct relationship between the IPR and entanglement breaks down. As a state becomes more and more mixed, the IPR stabilizes at a finite value, while entanglement drops towards zero. While both measures arrive at finite values, it should be clear that they do not differ by a simple factor or constant. We will see in §4 that they become qualitatively different.

(c) Coherence length

We can now rewrite Mukamel’s CL equation (3.8) in the language we have gained from entanglement:

$$\text{CL} \equiv \left( 1 + \sum_{m \neq n}^{N} \frac{C_{mn}(t)}{2} \right)^2 / \text{Tr}(\rho(t)^2)N.$$  \hspace{1cm} (3.17)

The main component of the numerator is the square of the sum of the inter-site concurrences. The denominator is simply the purity of the state times $N$. Now, the issues of the CL should become clear; owing to the presence of the purity in the denominator, the value of CL will decay far too slowly under decoherence, as $\text{Tr}(\rho(t)^2)$ tends to $1/N$. Moreover, given that the numerator involves the sum of the inter-site concurrences, the CL does not capture the monogamous nature of entanglement, unlike the tangle.

In §4, we present a comparison of the most commonly used delocalization measures, along with several entanglement measures, the use of which has recently gained popularity in the study of LHCs [1,15–18,49,63,64], where we use the B850 ring as a model system. This comparison will starkly illustrate the limitations of the CL.

4. The B850 ring of LH2

The photosynthetic complexes of purple bacteria have been subject to substantial analysis [3,65–73]. The light-harvesting apparatus of photosynthetic purple bacteria comprises two types of light-harvesting complex: LH1 and LH2. The LH1 forms a ring—either monomeric (closed ring) or dimeric (open, S-shaped ring)—that surrounds the RC [66], whereas the LH2 complexes are typically arranged around each LH1 [74,75]. The peripheral light-harvesting protein LH2 is assembled from subunits, each consisting of three bacteriochlorophyll-$a$ (Bchl-$a$) molecules: one carotenoid molecule, and two protein $\alpha$ helices (labelled $\alpha$ and $\beta$)
Figure 2. An illustration of the main light-harvesting components of *Rhodopseudomonas acidophila*, LH1 and LH2, and their respective intra and inter energy transfer times. This illustration was generated with VMD (Visual Molecular Dynamics) using Protein Data Bank (PDB) codes 1PYH and 2FKW. (Online version in colour.)

The subunits assemble into a ring, usually with ninefold rotational symmetry. The symmetry of the LH2 ring varies with the species of purple bacteria; *Rps. acidophila* is ninefold symmetric, with nine BChl-\(a\) molecules in the B800 ring and 18 in the B850 ring. *Rhodopseudomonas molischianum* is eightfold symmetric, with a similar subunit structure [76]. In this paper, we will focus on the LH2 complex of *Rps. acidophila*, the structure of which is known to a high resolution from X-ray crystallography [6]. Two spectrally distinct symmetric rings of BChl-\(a\) pigments result from the way the chromophores are arranged in the LH2 structure: B800 and B850. The B800 ring lies parallel with the cell membrane, whereas the B850 ring lies perpendicular to it. In the B800 ring, the BChl-\(a\) molecules are relatively far apart, with centre-to-centre distances in the region of 18–21 Å [28], causing excitations to be fairly localized [37]. By contrast, the B850 ring is formed by units of tightly packed overlapping dimers, leading to delocalized excitations. This excitonic effect, along with pigment–protein interactions [37], is what shifts the absorbance of the ring to 850 nm. The strongly coupled nature of the B850 ring has drawn much interest in the field [35–39,41,46,53,56], with many efforts to quantify the level of delocalization.

Within each LH2 subunit, there exists a carotenoid; the carotenoid molecules provide photoprotection for the system and also act as light-harvesting pigments, absorbing in the spectral window between the (Bchl-\(a\)) \(Q_x/Q_y\) and B bands [66].

Figure 2 provides an illustration of both the LH1 and LH2 complexes. Various energy transfer times are provided for the different possible scenarios. For example, consider an excitation arriving on the B800 ring: within roughly
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40 ps, the excitation travels from the B800 ring, up to the B850 ring, across to the LH1 ring, and eventually to the RC [66].

(a) Effects of inhomogeneous broadening on exciton states

We now turn our attention to measuring the delocalization of the exciton states of a disordered B850 ring. Allowing for different site energies $\epsilon_n$, and different inter-site couplings $J_{nm}$, we write out the electronic Hamiltonian as

$$H_e = \sum_n (\epsilon_n + D_n) |n\rangle\langle n| + \sum_{n=1}^{N} \sum_{m \neq n}^{N} J_{nm} |m\rangle\langle n|,$$

where $D_n$ is diagonal, static disorder that results in inhomogeneous broadening.

In the present paper, the Hamiltonian for the B850 ring of the LH2 is obtained from the site energies and electronic couplings calculated by Scholes et al. [77]. To analyse the level of delocalization in the B850 ring, we first generate an ensemble average (2000 iterations) of the Hamiltonian with a Gaussian distribution of static disorder at each site, with a standard deviation of 240 cm$^{-1}$ (approx. 2% of the site energy) to simulate inhomogeneous broadening. Figure 3 displays the B850 absorption spectrum, along with the IPR as a measure of the delocalization and the relative entropy as a measure of entanglement for the exciton states.

Figure 3. (a) Calculated absorption spectrum for the B850 ring, with the experimental absorption spectrum of the LH2 complex for comparison. Note that the experimental absorption spectrum also contains the B800 ring, hence the peak at 800 nm. (b) IPR and relative entropy for an ensemble of B850 exciton states, plotted against their eigenenergy. (Online version in colour.)
with respect to the exciton energy. There are several points of interest within this figure: firstly, we can see that, even under inhomogeneous broadening, most excitons remain delocalized, with the majority (approx. 70\%) of excitons having an IPR ranging from 1/18 to 1/2; secondly, the anti-correlation between the IPR and relative entropy is evident; and finally, it is interesting to note that the excitons concentrated around \( k = 0 \) (the lowest energy state of the homogeneous ring with no static disorder at 864 nm) are now strongly allowed, while the most delocalized states have a low transition strength.

(b) Dynamical localization: models for decoherence in EET

(i) Haken–Strobl model

In order to fully study the behaviour of these quantum measures, a dynamical model is needed. To get a qualitative description of EET in a given LHC, we first apply a simplified version [78] of the Haken–Strobl [79] model.

According to this model, site interaction with phonons leads to site energy fluctuations, which can be accounted for by the inclusion of a time-dependent term in the electronic Hamiltonian (equation (4.1)):

\[
H = \sum_n^N (\epsilon_n + D_n + \delta_n(t))|n\rangle\langle n| + \sum_{n=1}^N \sum_{m\neq n}^N J_{nm}|m\rangle\langle n|.
\]

The density matrix describing such a system is then subject to the Heisenberg equation of motion

\[
\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H, \rho].
\]

We assume there are no bath-induced correlations between sites, and that site energy fluctuations obey Gaussian–Markovian statistics such that

\[
\langle \delta_n(0)\delta_m(t) \rangle = \delta_{mn}\delta(t)\frac{1}{T_d},
\]

where \( T_d \) is the dephasing time. The resulting equations of motion are then

\[
\dot{\rho}_{nm} = -\frac{i}{\hbar} [H, \rho_{nm}] - \left( \frac{1}{T_d} \right) (1 - \delta_{nm})\rho_{nm}.
\]

This corresponds to a pure dephasing model in the site basis, where decoherence leads to an exponential decay of all coherences in the density matrix [80]. As time goes to infinity, all coherences vanish, and given that the Haken–Strobl model is based on a high-temperature approximation, the populations settle with equal probability, rather than a Boltzmann distribution, i.e.

\[
\lim_{t \to \infty} \left( \begin{array}{cccc}
\rho_{11}(t) & \rho_{12}(t) & \cdots & \rho_{1n}(t) \\
\rho_{21}(t) & \rho_{22}(t) & \cdots & \rho_{2n}(t) \\
\vdots & \vdots & \ddots & \vdots \\
\rho_{n1}(t) & \rho_{n2}(t) & \cdots & \rho_{nn}(t)
\end{array} \right) = \frac{1}{N} \left( \begin{array}{cccc}
1 & 0 & \cdots & 0 \\
0 & 1 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & 1
\end{array} \right).
\]

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Figure 4. Dynamic measures of coherence and purity in the B850 ring using the Haken–Strobl model, with initial state $k = -1$: (a) the B850 ring without disorder and (b) the B850 ring with static disorder. Here, we plot the decrease in purity (dashed green line), along with the total tangle $E_T$ (red line) and associated delocalization length—the IPR (the inverse of the delocalization length) as the blue line, and the CL as the black line. Note that, in both cases, the CL gives inflated values when the total tangle is negligible. (Online version in colour.)

To simulate EET in the B850 ring, we choose an optically bright exciton, $k = -1$ (an eigenstate of the system with no static disorder) as our initial state. The decoherence time is arbitrarily set to 50 fs, of the order of the transfer time within the B850 ring.

Within this model, we compare different metrics to quantify exciton delocalization in the B850 ring and investigate the effect of static disorder. Figure 4 plots several normalized quantum measures and the purity of the dynamic state, for a system (a) without and (b) with static disorder.

Figure 4 shows that in both cases (a) and (b) the purity (green dashed line) of the state shows a steady decline, indicating that the state evolves from a pure state ($\text{Tr}(\rho^2) = 1$) into a maximally mixed one ($\text{Tr}(\rho^2) = 1/N$), as expected from the pure dephasing model. To quantify entanglement, we use the total tangle, $E_T$ (equation (3.11)) (red line), which follows a similar trend and is nearly zero by 100 fs. We also analyse two more measures for exciton delocalization, the IPR (equation (3.4)) and the coherence length, CL (equation (3.8)), neither of which follow the same trend. The IPR (blue line) shows that the state begins highly delocalized; however, the IPR remains practically the same for the duration of the simulation, eventually matching the purity. This clearly demonstrates that the IPR is not suited to quantify delocalization in a dynamical scenario where the system becomes mixed as decoherence sets in. While the CL (black line) does eventually decay in both cases, it does so at a much slower rate than the total tangle, and still displays significantly large values by the time the total tangle reaches zero, before eventually reaching its asymptotic limit, $1/N$. Also, note that, in the case of static disorder, the CL fluctuates—this behaviour

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(ii) **Redfield model**

In order to apply a more detailed—yet simple—model for EET than the pure dephasing model, we use the Redfield equation within the secular approximation \([2,5,17,81]\). Once again, the entanglement and delocalization calculations are performed in the site basis. The density matrix of the system now obeys the following master equation:

\[
\frac{\partial \rho(t)}{\partial t} = -i[H_e, \rho(t)] + D(\rho(t)).
\]  

(4.7)

Here we have neglected the Lamb-shift-type Hamiltonian, which leads to a Lamb-type renormalization of the unperturbed energy levels induced by the system reservoir coupling. In this simulation, we also neglect inhomogeneous broadening. The first term on the right-hand side describes purely coherent evolution and the second induces dephasing and relaxation between excitonic states of the system through the dissipator operator \(D(\rho(t))\). The dissipator reads

\[
D(\rho(t)) = \sum_{\omega} \sum_{m,n} \gamma_{m,n}(\omega) \left[ A_n(\omega) \rho(t) A_m^\dagger(\omega) - \frac{1}{2} \{ A_m^\dagger(\omega) A_n(\omega), \rho(t) \} \right],
\]  

(4.8)

where \(A_n(\omega) = \sum_{\epsilon_{k'} - \epsilon_k = \omega} a_n^\dagger(\phi_k') a_n(\phi_k') |\phi_k')\langle \phi_k'|\) are the Lindblad operators, with \(a_n\) the site coefficients of exciton \(|\phi\rangle\) such that \(|\phi\rangle = \sum_n a_n |n\rangle\). We assume that energy fluctuations at different sites are not correlated and are site-independent. Consequently, the rates \(\gamma(\omega)\) are given by \(\gamma_{m,n}(\omega) = \gamma(\omega) \delta_{m,n} = 2\pi J(|\omega|) N(-\omega)\). \(J(\omega)\) is the spectral density characterizing the system–phonon coupling, which we assume to be ohmic with Drude cutoff, i.e. \(J(\omega) = 2E_r \omega_c \omega / \pi(\omega_c^2 + \omega^2)\), where \(E_r\) is the reorganization energy, \(\omega_c\) is the cutoff frequency and \(N(\omega)\) is the thermal occupation number.

Once more, we choose exciton \(k = -1\) as our initial state, and set the reorganization energy \(E_r\) to 200 cm\(^{-1}\) \(\langle 56\rangle\), the cutoff frequency \(\omega_c\) to 300 cm\(^{-1}\) \(\langle 56\rangle\) and the temperature \(T\) to 293 K.

In figure 5, we present the exciton population and coherence dynamics for a simulation lasting 500 fs. Within this model, the system relaxes towards a thermal equilibrium where exciton populations obey a Boltzmann distribution. Figure 5b shows the CL, the total tangle and the relative entropy as measures of quantum coherence (in the site basis), together with the purity as a measure of mixedness in the state. As can be seen, the resulting state is not completely mixed and there remains some finite level of coherence in the system, which comes from the coherences within the exciton states. The entanglement measures of total tangle and relative entropy both follow a similar trend, displaying a smooth decay in time. Instead, once more, the CL displays an unusual behaviour by remaining static for the first 50 fs, before eventually decreasing and settling on a lower-than-initial value of 0.4.
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Figure 5. Dynamics of the B850 ring at 293 K with initial state of $k = -1$, using the Redfield model with secular approximation. (a) The time evolution of the largest exciton populations, eventually reaching a Boltzmann distribution at 250 fs. (b) The time evolution of the quantum measures in the site basis, all reaching some finite value. (Online version in colour.)

Figure 6. Dynamics of the B850 ring at 77 K with initial state of $k = -1$, using the Redfield model with secular approximation. (a) The time evolution of the largest exciton populations, eventually reaching a Boltzmann distribution at 1 ps. (b) The time evolution of the quantum measures in the site basis. (Online version in colour.)

To further demonstrate the limitations of the CL in quantifying quantum coherence, we can examine the system dynamics at the low temperature of 77 K; first with the initial state $k = -1$, as mentioned earlier, and then with the excitation localized on site 1. In figure 6b, we see an even greater contrast between the CL and the total tangle, as the CL varies little for the first 400 ps, while the total tangle decays with decoherence. As the populations reach equilibrium (figure 6a), the CL and other coherence measures become correlated. Changing
Figure 7. Dynamics of the B850 ring at 77 K with initial state of site 1. (a) The time evolution of exciton populations, with exciton \( k = 0 \) dominating by 500 fs. (b) The time evolution of the quantum measures in the site basis; note the marked contrast between the CL and the two entanglement measures. (Online version in colour.)

Our initial state to the excitation localized on site 1, the excitation begins in a coherent superposition of excitons, as shown in figure 7. As the system relaxes over time, the majority of the excitation rests in the lowest-level energy state, exciton \( k = 0 \) (figures 6a and 7a). Some of the measures in figure 7b reflect this; for example, the purity increases as the state begins to localize on \( k = 0 \). Therefore, as a coherent superposition of sites is formed, the entanglement measures increase.

Initially, the CL exhibits behaviour similar to levels of entanglement, showing that, for low temperatures and at very short time scales, it provides a good sense of the degree of delocalization in the system. However, after 0.04 ps, it begins to climb sharply, then oscillates, first fluctuating rapidly, then flat-lining for a short period, before eventually increasing at 0.2 ps. By referring back to equation (3.8), one can explain this peculiar behaviour by the rate of change of purity, and the rate of change of the total tangle (the square of the concurrence). When the purity and total tangle curves have similar slopes, the CL flat-lines. If the total tangle is mildly oscillating, then the decaying purity, as the numerator, amplifies these oscillations. This is why we see increasing and fluctuating values as the total tangle decreases, and static values as the total tangle increases.

It is worth noting that, for all of the earlier-mentioned coherence figures, the relative entropy often returns a higher value of coherence than the total tangle; this is because they are fundamentally different functions; the relative entropy is logarithmic, whereas the total tangle is quadratic. No matter, these functions share the same limits, in that they report zero for a separable state, and \( 1/N \) for a fully delocalized state. So, while the relative entropy is quantitatively different from the total tangle, it does not differ qualitatively, unlike the CL. However, given the inverse relationship between total tangle and the IPR for pure states, the total tangle is probably a better candidate for the measurement of electronic coherence.

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5. Conclusions

Dynamical simulations of energy transfer and the time evolution of excitonic states in the B850 ring of the LH2 complex from purple bacteria provided an excellent case study for comparing measures that aim to quantify the degree of delocalization in a quantum state. In this work, we have focused on contrasting the traditionally used inverse participation quantities, intended to provide an exciton delocalization length in the system under study, with entanglement measures that are able to quantify the distribution in space and time evolution of exciton delocalization. Often these two metrics are interconnected, and participation ratios can be rewritten as functions of entanglement measures such as the concurrence and the tangle (equations (3.11) and (3.17)). We found that equivalence between participation and entanglement measures is valid only in the case of pure states. Under decoherence, they serve different purposes: the IPR (equation (3.4)) no longer returns meaningful results, except perhaps for states with no coherence where it becomes a measure of classical entropy, whereas entanglement remains purely a measure of delocalization. In other words, within the regime of a pure state or a fully classical state, participation ratios are perfectly suitable to quantify delocalization and entropy, respectively. However, as a dynamic measure for coherence, entanglement is clearly preferred. Moreover, the distribution of entanglement better describes the distribution of coherence by focusing solely on the quantum correlations. The CL, although equipped to measure the evolution of coherence (unlike the IPR), is somewhat unreliable, both qualitatively and quantitatively; its long-term evolution does not represent that of the system’s coherence, and it often exhibits values far inflated above their true nature. In contrast, the total tangle and relative entropy provide accurate readings of quantum coherence for any time scale and temperature. The typical IPR remains an incredibly useful measure; yet there should be a place for new measures from quantum information, as they are more effective at characterizing delocalization in multi-chromophoric systems under decoherence.

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