

A critical view on transport and entanglement in models of photosynthesis

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We revisit critically the recent claims, inspired by quantum optics and quantum information, that there is entanglement in the biological pigment–protein complexes, and that it is responsible for the high transport efficiency. While unexpectedly long coherence times were experimentally demonstrated, the existence of entanglement is, at the moment, a purely theoretical conjecture; it is this conjecture that we analyse. As demonstrated by a toy model, a similar transport phenomenology can be obtained without generating entanglement. Furthermore, we also argue that, even if entanglement does exist, it is purely incidental and seems to play no essential role for the transport efficiency. We emphasize that our paper is *not* a proof that entanglement does not exist in light-harvesting complexes—this would require a knowledge of the system and its parameters well beyond the state of the art. Rather, we present a counter-example to the recent claims of entanglement, showing that the arguments, as they stand at the moment, are not sufficiently justified and hence cannot be taken as a proof for the existence of entanglement, let alone of its essential role, in the excitation transport.

Keywords: entanglement; quantum coherence; photosynthesis

1. Introduction

In recent years, following the development of quantum information, the phenomenon of quantum entanglement has been identified as being one of the most important aspects of quantum mechanics. It was realized that the presence of entanglement confers quantum systems significantly enhanced power for accomplishing many tasks [1], such as exponentially increased speed-up of computation and significantly enhanced communication capacity. As such, it has been very natural to enquire whether biological systems could have evolved to make use of entanglement. Recently, the importance of investigating this question received a major impetus following seminal experiments that indicated

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the existence of unexpectedly long-time coherent effects in photosynthesis [2–4]. Since coherence is a prerequisite for entanglement, its discovery raises the possibility that entanglement is also present. Moreover, it is known that the energy transport in light-harvesting complexes is extremely efficient. Could it be the case that entanglement is responsible for this efficiency? A few groundbreaking studies [5,6], followed by an increasing body of literature [7–12], raised this question and suggested that this is the case. Here, we take a critical look at these results.

The main issue to be discussed here is that of coherence versus entanglement. They are definitely not one and the same thing. The existence of entanglement is a stronger criterion than the presence of coherence. That is, entanglement requires the presence of coherence, but coherence does not imply entanglement in general. While coherent phenomena can also appear in systems of classical wave mechanics, entanglement is a genuine quantum phenomenon, which is required to violate a Bell inequality, for example.

It is important to mention from the beginning that, while the existence of coherence in light-harvesting systems has been experimentally tested (at least in laboratory conditions), the existence of entanglement has not. This is not surprising—experimentally proving entanglement is a far more difficult task [13]. As such, all the discussion about entanglement in light-harvesting systems is, at present, purely theoretical.

The existence of coherence in these systems seems now to be well established, and we are not challenging that. It is also quite reasonable to expect that coherence plays an important role in the transport problem, distinguishing it from classical diffusive processes; we are not challenging this either. What concerns us here is the existence of entanglement and its role, if it exists. Specifically, the main questions we address in our paper are as follows:

- Are the assumptions that lead to the present claims of entanglement in photosynthesis justified?
- Even if these assumptions are justified and entanglement does exist along the lines of those models, does the entanglement play any significant role in enhancing the efficiency of transport or it is of no consequence?

We suggest that, despite the sizable body of literature claiming the contrary, the answer to both questions is ‘no’.

To be clear, we do not prove that there is no entanglement in photosynthesis. To do that, we would require knowledge of the system that is well beyond what is available at present. All we do here is to present arguments that point to potential problems in the present claims that entanglement exists and plays a significant role. Our paper should rather be viewed as a counter-example and it is meant to sharpen the further investigation of the problem.

2. Basic issues

Light-harvesting complexes in plants and photosynthetic bacteria comprise protein scaffolds into which pigment molecules are embedded, e.g. chlorophyll or bacteriochlorophyll molecules. The pigment molecules absorb light in the visible

or infrared part of the spectrum, and the resulting electronic excitation (exciton) is transported between the pigment molecules until it reaches a reaction centre complex, where its energy is converted into separated charges.

The Fenna–Matthews–Olson (FMO) protein complex of green sulfur bacteria is a trimeric complex that links the chlorosome antenna with the reaction centre. Within each of the subunits, there are seven chlorophyll molecules in close connection with each other. Each of these molecules can be considered as a ‘site’ where the excitation propagating from the chlorosome to the reaction centre may be localized. It is the entanglement between these sites during the propagation of excitation that is discussed in the earlier studies [5–11]. (Alternatively, the so-called ‘mode’ entanglement has also been considered in the study of Caruso *et al.* [9]. There, the physical systems between which entanglement is investigated are no longer identical to the pigment cofactors but effective systems that are defined by the single-excitation spectrum of the Hamiltonian of the coupled pigments.)

Regarding the existence and generation of entanglement in light-harvesting complexes, we draw some intuition from the following formal analogy. As we will detail later, to a certain extent, the FMO complex can be seen as analogous to a multi-armed interferometer, where each interferometer arm corresponds to a site in the FMO complex. The propagation of a single excitation through the FMO complex is then analogous to the propagation of a single photon through the interferometer. A single photon propagating through an interferometer can indeed immediately lead to entanglement between the arms [14]; hence, from this point of view, it is not very surprising that a single excitation propagating through the FMO complex may lead to entanglement between sites. However, and this is one of our main concerns, if instead of a single photon we send a coherent state through the interferometer, then no arm entanglement will appear at all. Indeed, at a beam splitter, a coherent state is split into a product of coherent states in each of the outgoing arms. As the light passes the various beam splitters in the interferometer, in each step we maintain a direct product of coherent states in each of the arms. We stress that this is true even for very weak coherent states where the probability of having more than a single photon is overwhelmingly small.

There are two lessons to be learned from this analogy. First, whether or not entanglement between interferometer arms exists depends crucially on the initial state. Our concern is that, in the case of photosynthesis, in which the entire light-harvesting complex is illuminated by weak classical light and not single photons, entanglement may therefore not appear inside the FMO complex.

The second lesson is that the actual dynamics of light propagation through an interferometer, and hence a measure of the transport efficiency, does not really depend on the fact that, at single-photon level, entanglement between arms is produced. Indeed, the dynamics of an interferometer can very well be described at classical level, i.e. via coherent states, where the question of entanglement does not appear. Hence, we conclude that entanglement beyond the mere existence of coherences, although it does appear at single-photon level, is irrelevant for the light transport in interferometers.

However, excitation transport in the FMO complex is not exactly identical to light propagation in an interferometer. It is therefore important to see whether or not the problems we mentioned earlier are still relevant for

excitation propagation through light-harvesting complexes. In this paper, we argue that, indeed, entanglement plays no essential role in transport through the FMO complex.

Following from the discussion above, we thus need to revisit the general assumptions that have been made in existing theoretical treatments of entanglement in light-harvesting complexes, in particular the following points:

- the initial state entering the complex; and
- the transport between sites and the possible entanglement generated thereby.

More specifically, we also reconsider the modelling of each of the sites as a simplified two-level system.

3. Initial excitation

The available literature on entanglement generated during excitation transport in pigment–protein complexes usually assumes an initial state where (i) *only one* site is excited and (ii) this site is excited with exactly one quantum of electronic excitation, i.e. a ‘Fock state’, as done in the earlier works [5,6,8], for example. Given these assumptions, the pigments of the light-harvesting complex have been modelled by two-level systems, corresponding to the presence or absence of an excitation at that location.

The rationale behind the above assumption for the initial state is often the following. Under illumination by sunlight or, in experiment, by femtosecond laser pulses, the photon flux per pigment is weak. An estimation for conditions in full sunlight yields a value of about 10 absorbed photons per chlorophyll molecule per second in the relevant part of the spectrum [15]. Considering that the typical time scale for exciton transport is of the order of picoseconds, with exciton lifetimes of nanoseconds, this suggests that *if* light is absorbed, then most probably only one excitation is present.

However, our main point is that the light that excites the light-harvesting apparatus is essentially classical, technically a mixture of coherent states. Importantly, even if a coherent state is very weak, and the probability of containing more than one excitation is very low, this by no means implies that it can be described as a single-excitation Fock state. Hence, using the weakness of the incident light as an argument for modelling the initial state as a Fock state is a fallacy.

A coherent state differs from a Fock state in two important aspects. First of all, a coherent state contains not only one excitation but also terms with more excitations. Second, the coherent state also contains a term, the vacuum, without excitations. In particular, the existence of the vacuum term has interesting consequences. It is completely irrelevant as far as the dynamics of excitation transport is concerned—it just represents the fact that nothing happens—but it has crucial implications for entanglement. Since the entanglement that is considered in light-harvesting systems stems from superpositions of states in which one pigment is excited and all others are in the ground state, a contribution with all pigments being in the ground state, corresponding to the vacuum in the incoming light, plays an essential role and must not be neglected.

At this point another possibility arises, namely, that the initial state in the *FMO complex* that is of interest for us could be a Fock state for reasons other than the weakness of the incident light. Indeed, the *FMO complex in vivo* is not directly excited by the incident light; rather, it receives its input through the antenna complex. It is thus conceivable that some mechanism in the antenna and its connection to the *FMO complex* may somehow generate a Fock state. In quantum-mechanical terms, this amounts to a state preparation process. What would this require?

Producing a Fock state in the *FMO complex* would require two things. On the one hand, it should cut the possibility of more than one excitation. Such mechanisms have been discussed [16], although it is not clear to us how efficient they are in limiting the number of higher excitations within the time frame that is relevant for transport through light-harvesting complexes. On the other hand, to produce a Fock state, one should also be able to eliminate the vacuum component of the state. To our knowledge, no such mechanism has been suggested so far.

This entire discussion above is highly relevant since, as far as entanglement is concerned, the difference between coherent states, even if they are extremely weak, and one-photon Fock states is dramatic. While one-photon Fock states may result in entanglement between linearly coupled systems, coherent states will not. Furthermore, even in nonlinearly coupled systems, weak coherent states can only produce very limited amounts of entanglement, far below that produced by one-photon Fock states.

4. Harmonic oscillator model

Having discussed the difference between the initial states, we now explicitly illustrate the difference that the two states make regarding entanglement.

In existing studies of entanglement in light-harvesting complexes, the manifold of electronic states of each of the relevant pigments, e.g. chlorophyll molecules, is usually restricted to only a few levels, mostly only the electronic ground state and the first excited state. The rich energetic landscape of each chlorophyll molecule is thereby conceptually replaced by a two-level atom.

In order to account for small contributions of higher-excited states, we must consider a different model for the electronic level structure of each pigment molecule that allows for more excitations to be present at a single site. As the simplest possible scenario, consider the analogy of a light-harvesting complex to an interferometer. In this analogy, the electronic level structure of each site is modelled by a harmonic oscillator, and thus it is formally identical to a light mode in an interferometer.

For capturing the principles of entanglement generation during the evolution of the excitations in a network of coupled chlorophyll pigments, it is sufficient to first study the interaction and state evolution of the simplest network of only two sites, a dimer. Hence, we first consider how entanglement is generated between two coupled harmonic oscillators. (Incidentally, the present approach to model the pigment molecules by harmonic oscillators has also been employed in the study of Briggs & Einfeld [17]; however, by means of *classical* harmonic oscillators and with a different aim, namely to illustrate that the phenomenology of quantum

coherent exciton transport can also be obtained with a classical coherent model. In the present work, however, we employ a full quantum description, and our focus lies on entanglement.)

We assume for the interaction Hamiltonian a standard form where excitations are exchanged between the modes, the rotating-wave approximation has already been applied, and the systems are taken to be resonant:

$$H_{\text{int}} = g\hbar(a^\dagger b + ab^\dagger). \quad (4.1)$$

The coupling strength is denoted by g , and the creation and annihilation operators a , b and a^\dagger , b^\dagger for the harmonic oscillators describing molecules A and B, respectively, realize the exchange of an excitation between the molecules.

To exemplify our argument with coherent states, we investigate the initial state of a coherent state for molecule A, which expanded into the Fock basis of states with n excitations reads

$$|\psi_A(0)\rangle = |\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle, \quad (4.2)$$

and whose mean number of excitations is given by $|\alpha|^2$. For molecule B, we take the vacuum (ground) state $|\psi_B(0)\rangle = |0\rangle$. The requirement that the light intensity is low and hence an excitation occurs only with small probability, and that higher-excited states should virtually not occur, thus formally amounts to $|\alpha| \ll 1$ for the initial state. This initial state is in accordance with the central assumption that *if* an excitation occurs, then most probably there is only a single excitation, because for $n > 1$

$$|\langle 1|\psi_A(0)\rangle|^2 = e^{-|\alpha|^2} |\alpha|^2 > \frac{e^{-|\alpha|^2} |\alpha|^{2n}}{n!} = |\langle n|\psi_A(0)\rangle|^2. \quad (4.3)$$

In the interferometer analogy, this initial state amounts to a coherent state and a vacuum state for the two incident light modes, respectively.

Under the given Hamiltonian, the state of the two molecules evolves in the interaction picture according to

$$|\psi_{AB}(t)\rangle = U(t)|\psi_A(0)\rangle|\psi_B(0)\rangle = e^{-igt(ab^\dagger + a^\dagger b)} |\alpha\rangle |0\rangle. \quad (4.4)$$

The time evolution of this system of two coupled harmonic oscillators is an elementary problem. A standard textbook calculation yields [18]

$$|\psi(t)\rangle = U(t)D_A(\alpha)U^\dagger(t)U(t)|0\rangle|0\rangle \quad (4.5)$$

$$= e^{\alpha Ua^\dagger U^\dagger - \alpha^* UaU^\dagger} |0\rangle|0\rangle. \quad (4.6)$$

Here, the displacement operator $D_A(\alpha) = \exp(\alpha a^\dagger - \alpha^* a)$ is used to construct coherent states by simply moving the ground state (vacuum) away from the phase space origin, $|\alpha\rangle = D_A(\alpha)|0\rangle$. The unitarity of $U(t)$ allows one to sandwich all operators in the exponential by inserting identity operations, the time argument

has been omitted, and the ground state is invariant under U . Using the relation

$$e^X Y e^{-X} = Y + [X, Y] + \frac{1}{2!}[X, [X, Y]] + \frac{1}{3!}[X, [X, [X, Y]]] + \dots, \quad (4.7)$$

the sandwiched creation and annihilation operators can be evaluated

$$U a^\dagger U^\dagger = \cos(gt) a^\dagger + i \sin(gt) b^\dagger \quad (4.8)$$

and

$$U a U^\dagger = \cos(gt) a - i \sin(gt) b. \quad (4.9)$$

Since the operators for molecules A and B commute, the exponential can be split into two parts that each give a displacement operator for molecules A and B, respectively,

$$\begin{aligned} |\psi(t)\rangle &= D_A[\alpha \cos(gt)] D_B[i\alpha \sin(gt)] |0\rangle |0\rangle \\ &= |\alpha \cos(gt)\rangle |i\alpha \sin(gt)\rangle. \end{aligned} \quad (4.10)$$

In the final state, after some interaction time t , each of the two molecules is in a coherent state with parameters $\alpha \cos(gt)$ and $i\alpha \sin(gt)$, respectively. With respect to entanglement, let us point out that, for all interaction times and irrespective of α , the two molecules are always in a product state, i.e. there is strictly no entanglement between the molecules.

Let us spell out the formal analogy between the dynamics in our simplified model of the two interacting chlorophyll molecules, the electronic structure of each of which is modelled by a harmonic oscillator, and two light modes interacting at a beam splitter. At a beam splitter, in the Schrödinger picture, the state of the two incident and outgoing light modes $|\phi_{\text{in}}\rangle$ and $|\phi_{\text{out}}\rangle$, respectively, is related by a unitary operation [19], which contains the reflectivity/transmissivity of the beam splitter as a parameter θ :

$$|\phi_{\text{out}}\rangle = U(\theta) |\phi_{\text{in}}\rangle = e^{-i(\theta/2)(a^\dagger b + ab^\dagger)} |\phi_{\text{in}}\rangle. \quad (4.11)$$

The unitary operation of the beam splitter is formally identical to that of the two interacting molecules in (4.4). Therefore, the state of the molecules before and after they have interacted for some time t can be associated with the state of the two light modes before and after they have passed the beam splitter with reflectivity/transmissivity parameter $\theta/2 = gt$. A 50:50 beam splitter with $\theta = \pi/2$ thus gives states in the output ports that correspond to the states of the molecules after time $gt = \pi/4$: for an initial coherent state, one obtains a product of coherent states as in (4.10). In contrast, for a single photon entering the beam splitter in one input port, $|\phi_{\text{in}}\rangle = |10\rangle$, the state emerging from the beam splitter is $|\phi_{\text{out}}\rangle = (|10\rangle + i|01\rangle)/\sqrt{2}$, a maximally entangled state of the two interferometer arms.

Let us translate the observation of a coherent state versus a single-photon Fock state from the interferometer analogy back to the model system of interacting pigment molecules. Given that the initial state is a coherent state, the act of

limiting the focus of the treatment to the single-excitation manifold creates the *illusion* of entanglement. Formally, one projects the total state (4.10) to the subspace with exactly a single excitation and obtains for the initial state

$$P_1|\alpha\rangle|0\rangle \propto |10\rangle, \quad (4.12)$$

where

$$P_1 = |10\rangle\langle 10| + |01\rangle\langle 01| \quad (4.13)$$

is the projection onto the single-excitation subspace. That is, there is one excitation on molecule A and none on B. For the time-evolved state, this projection yields

$$P_1|\psi_{AB}(t)\rangle = P_1|\alpha \cos(gt)\rangle|i\alpha \sin(gt)\rangle \propto \cos(gt)|10\rangle + i \sin(gt)|01\rangle. \quad (4.14)$$

In particular, for $gt = \pi/4$, the state appears to be maximally entangled in analogy to a single photon traversing a 50:50 beam splitter.

It is interesting to ask: Why does considering all possible excitations remove the entanglement? How can the higher-excitations sector, which has a very small contribution, remove the entanglement? This seems to be quite paradoxical. The answer is that, if the coherent state is so weak as to have only a very small amount of higher excitations, it necessarily also has a very large vacuum component. Just considering the vacuum term in addition to the single-excitation sector reduces the amount of entanglement considerably. Any residual entanglement is eliminated by the higher-excitation sector.

To see the effects from above, it is convenient to use a measure of the amount of entanglement as given by the concurrence [20], which for a pure state of two systems is defined in terms of the purity of one (any) of the subsystems:

$$C(|\psi_{AB}\rangle) = \sqrt{2(1 - \text{Tr}\rho_A^2)} \quad \text{with} \quad \rho_A = \text{Tr}_B|\psi_{AB}\rangle\langle\psi_{AB}|. \quad (4.15)$$

The concurrence of the (renormalized) state after projecting out the single-excitation sector gives

$$C\left(\frac{P_1|\psi_{AB}\rangle}{\|P_1|\psi_{AB}\rangle\|}\right) = |\sin(2gt)|, \quad (4.16)$$

which is maximal for $gt = \pi/4$.

Alternatively, if the attention is not strictly limited to the single-excitation manifold but the vacuum (ground-state) term is considered in addition, the relevant projection to apply to the state is

$$P_{0,1} = |00\rangle\langle 00| + P_1. \quad (4.17)$$

For the initial state, this projection yields a superposition of the ground and excited states of the first site, i.e.

$$P_{0,1}|\psi_{AB}(0)\rangle = P_{0,1}|\alpha\rangle|0\rangle \propto (|0\rangle + \alpha|1\rangle)|0\rangle, \quad (4.18)$$

and, for the time-evolved state, a superposition of the ground state and the evolved state in the single-excitation manifold, i.e.

$$P_{0,1}|\psi_{AB}(t)\rangle \propto |00\rangle + \alpha\{\cos(gt)|10\rangle + i\sin(gt)|01\rangle\}. \quad (4.19)$$

The entanglement in terms of concurrence of the normalized state is therefore

$$C\left(\frac{P_{0,1}|\psi_{AB}\rangle}{\|P_{0,1}|\psi_{AB}\rangle\|}\right) = \frac{|\alpha|^2}{1+|\alpha|^2}|\sin(2gt)|. \quad (4.20)$$

We find that the maximal amount of entanglement at $gt = \pi/4$ is limited by the dominant ground-state contribution for small $|\alpha|$, because the ground-state is not entangled.

The entanglement that appears after projecting the state onto its zero- and single-excitation subspace with $P_{0,1}$ is simply rescaled with respect to the entanglement found when projecting only to the single-excitation manifold. The scaling factor $|\alpha|^2/(1+|\alpha|^2)$ amounts to the single-excitation fraction of the projected state, i.e. the probability of measuring exactly a single excitation in the state once it has been projected. As long as the assumption holds that the probability of more than one excitation is small, we require that also $|\alpha|$ is very small, and therefore the entanglement reduction due to the ground-state contribution is larger. The higher-excitation terms in the coherent state may be small in absolute magnitude, but they only have to eliminate this weak residual entanglement.

Another aspect that needs to be taken into account when advancing to more realistic models for the study of quantum entanglement in light-harvesting complexes is that superpositions of electronic states on the same molecule may suffer from *decoherence*, primarily due to the coupling of the electronic structure to nuclear degrees of freedom. This process ultimately turns a coherent state

$$\rho_A(0) = |\psi_A(0)\rangle\langle\psi_A(0)| = |\alpha\rangle\langle\alpha|, \quad (4.21)$$

when written as a density operator, into the incoherent mixture

$$\rho_A(t \rightarrow \infty) = e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} |n\rangle\langle n| \quad (4.22)$$

of electronic states of the individual molecule, meaning that, after complete decoherence, all coherences between states of different excitation number will have decayed. At room temperature, molecules have been demonstrated to remain in a coherent superposition of their electronic ground and first excited states for a 50 fs time scale [21], which might, however, differ for pigment molecules embedded in a protein matrix.

In the worst case, a complete decoherence of an initially coherent state and subsequent projection to ground and single-excited manifold yields the incoherent mixture of the ground state and the coherently propagated single excitation:

$$\begin{aligned} \rho_{0,1}^{(\text{decoh})}(t) &= \frac{1}{1+|\alpha|^2} \{ |00\rangle\langle 00| + |\alpha|^2(\cos(gt)|10\rangle + i\sin(gt)|01\rangle) \\ &\quad \times (\cos(gt)\langle 10| - i\sin(gt)\langle 01|) \}. \end{aligned} \quad (4.23)$$

The concurrence for this mixed density matrix can be evaluated with Wootters' formula [20], and gives

$$C(\rho_{0,1}^{(\text{decoh})}(t)) = \frac{|\alpha|^2}{1 + |\alpha|^2} |\sin(2gt)|, \quad (4.24)$$

that is, the same result as for the projected coherent state (4.20).

5. N -level system model

After we have formally established that the molecules are not entangled if the initial state is a coherent state, and that a projection of the state to the single-excitation manifold creates the illusion that entanglement were present, let us now investigate how the number of considered levels in addition to the ground state and the single-excited state affects the apparent amount of entanglement. In other words, we generalize from the projections P_1 and $P_{0,1}$ of the previous section to projections that include a higher number of excitations.

An alternative way to look at this question is the following consideration. The electronic eigenstates of molecules do not form an infinite uniform level structure as a harmonic oscillator. It is reasonable to assume that only finitely many excitations can be supported by each pigment molecule, and any number of excitations beyond a certain threshold would cause ionization processes that take this fraction of the state out of the considered events. For example, instead of a coherent state at one of the molecules, which involves contributions of arbitrarily many excitations, the molecule may at most support two excitations. The initial state would thus be the first three terms of the coherent state expansion until $n = 2$:

$$|\psi_A^{(3)}(0)\rangle = \frac{1}{1 + |\alpha|^2 + |\alpha|^4/2!} \left(|0\rangle + \alpha|1\rangle + \frac{\alpha^2}{\sqrt{2!}}|2\rangle \right), \quad (5.1)$$

which corresponds to the projection $P_{0,1,2}$ applied to the coherent state $|\alpha\rangle$, and the result renormalized. For these kinds of initial states, which constitute a modification of coherent states towards a more realistic initial state for pigment molecules, we now study how the number of additionally considered contributions of higher-lying excited states affects the amount of entanglement that is generated during the transfer of excitations between two pigment molecules. Clearly, for the highest considered excited state being $N = 1$, we recover the result (4.20), whereas in the limit $N \rightarrow \infty$ we recover the case of coherent states that never generate entanglement.

In general, we model each molecule by a system of N levels, i.e. the ground state and $N-1$ excited states. In parallel with the harmonic oscillator, we choose the initial state to be the ground state for molecule B, and a state for molecule A,

$$|\psi_A^{(N)}(0)\rangle = |\alpha_N\rangle = \frac{1}{\sqrt{\mathcal{N}_{\alpha,N}}} \sum_{n=0}^{N-1} \frac{\alpha^n}{\sqrt{n!}} |n\rangle, \quad (5.2)$$

that is the projection of a coherent state to the lowest-lying N levels. The squared norm $\mathcal{N}_{\alpha,N} = \sum_{n=0}^{N-1} |\alpha|^2/n!$ approaches the value $e^{|\alpha|^2}$ found for coherent states in the limit $N \rightarrow \infty$.

As another exemplary case, let us give the analytic expressions for $N = 3$ for the initial state (5.1) as it evolves according to the interaction Hamiltonian (4.1). The time-evolved state necessarily contains only terms with at most two excitations:

$$|\psi_{AB}^{(3)}(t)\rangle = \frac{1}{\sqrt{1 + |\alpha|^2 + |\alpha|^4/2}} \left\{ |00\rangle + \alpha(\cos(gt)|10\rangle - i\sin(gt)|01\rangle) + \frac{\alpha^2}{\sqrt{2}}(\cos^2(gt)|20\rangle - \sin^2(gt)|02\rangle - i\sqrt{2}\cos(gt)\sin(gt)|11\rangle) \right\}. \quad (5.3)$$

For $|\alpha| \ll 1$, the doubly excited states give only a perturbative correction to the expression of the quantum state for the case $N = 2$ in (4.19). The expression for entanglement, however, not only changes by a perturbative correction, but also changes considerably. The concurrence of the state is given by

$$C(|\psi_{AB}^{(3)}\rangle) = \frac{|\alpha|^3 |\sin(2gt)| \sqrt{8 + (1/2)|\alpha|^2(13 + 3\cos(4gt))}}{4(1 + |\alpha|^2 + |\alpha|^4/2)}, \quad (5.4)$$

with its maximum at $gt = \pi/4$ of

$$C_{\max}^{(3)} = \frac{|\alpha|^3 \sqrt{8 + 5|\alpha|^2}}{4(1 + |\alpha|^2 + |\alpha|^4/2)}. \quad (5.5)$$

The expression of concurrence for $N = 3$ is similar in structure to that of the case $N = 2$ in (4.20), with a $|\sin(2gt)|$ modulation in time, and the squared norm of the projected coherent state in the denominator. The time-independent prefactor, however, can no longer be interpreted as the probability of having an excitation in the system, as done for $C_{\max}^{(2)}$ in (4.20). Instead, we find a scaling with the third power of $|\alpha|$.

Expressions for larger N can be straightforwardly obtained, but are omitted here. We have analytically examined expressions for the concurrence up to $N = 7$ and generally find a global $|\sin(2gt)|$ modulation in time in accordance with the intuition that maximal entanglement for these initial states is reached for the 50:50 beam splitter configuration, that is, after half the time that an excitation needs to move fully from one pigment to the other. In particular, the expressions for maximal entanglement are of the generic form

$$C_{\max}^{(N)} = \frac{|\alpha|^N}{\mathcal{N}_{\alpha,N}} f_N(|\alpha|^2), \quad (5.6)$$

that is, the apparent amount of entanglement decreases exponentially with the number of considered levels per molecule for $|\alpha| < 1$. The factor f_N for higher N is of a similar square root form as found for $N = 3$. For $|\alpha| < 1$, the leading term of $f_N(|\alpha|^2)$ is constant but also decreases with N , as listed in table 1. Figure 1 shows how the maximal apparent amount of entanglement decreases with N for various choices of α .

Obviously, the interpretation that, given an initial coherent state for $|\alpha| \ll 1$, one arrives at the single-photon level is misleading because the entanglement properties of a single-photon Fock state are not obtained in this limit. Instead, for

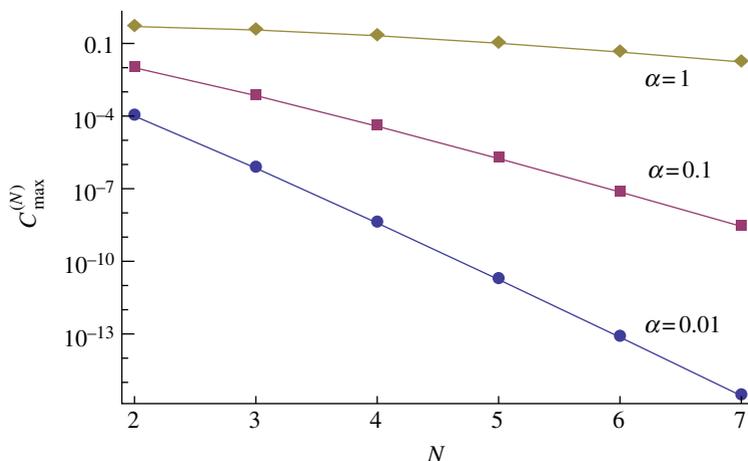


Figure 1. Scaling of maximal value of apparent entanglement as measured by concurrence, $C_{\max}^{(N)}$, for different α as a function of the number of considered N levels. (Online version in colour.)

Table 1. Constant leading-order terms of $f_N(|\alpha|^2)$ for $|\alpha| \ll 1$.

N	2	3	4	5	6	7
$f_N \approx$	1	$\frac{1}{\sqrt{2}}$	$\frac{1}{4}\sqrt{\frac{7}{3}}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{24}\sqrt{\frac{31}{10}}$	$\frac{1}{16\sqrt{5}}$
\approx	1	0.7071	0.3819	0.1768	0.0734	0.0280

smaller values of $|\alpha|$, the apparent entanglement will vanish more rapidly when increasingly many levels of the system are taken into account although they contribute to an ever smaller extent (figure 1).

We have also investigated an alternative way of modelling the initial state of an N -level molecule by means of *atomic* coherent states (also called *spin* coherent states) [18,22], where, instead of the raising and lowering operators of the harmonic oscillator, those of the angular momentum algebra are employed. The N levels of each molecule are thereby modelled by the $N = 2s + 1$ levels of an effective spin- s particle. Although the computations are more intricate due to the different commutation relations, we arrive at qualitatively similar results as presented for the projected harmonic oscillator. We therefore conclude that our argument concerning the entanglement content of a system that starts in a coherent state is robust with respect to the specific framework applied.

6. Transport efficiency versus entanglement

The *excitation transfer efficiency* in chromophore complexes captures how well an excitation that starts somewhere localized in the complex traverses the network of coupled chromophores to a different location, where it is assumed to leave the complex, e.g. to the reaction centre. A question of current interest that has been addressed [8,11] is whether or not entanglement (rather than mere coherence) impacts the transport efficiency.

Let us first recollect a few essential facts about the recent treatments of excitation propagation and the evaluation of transport efficiency in conjunction with the study of entanglement in light-harvesting complexes. In a complex of coupled chromophores with pairwise interaction Hamiltonians of the kind as in (4.1), the number of excitation quanta is conserved. Subspaces of a fixed number of excitation quanta, e.g. the single-excitation subspace, therefore evolve independently from each other. Cross-contributions of subspaces with a fixed excitation number occur only due to interaction of the chromophores with other degrees of freedom, i.e. an environment, and for the excitation energies considered here (approx. 1 eV) mostly downwards to lower numbers of excitation, owing to relaxation, for example. Given that the assumption holds that the light intensity is weak and therefore the presence of a higher number of excitations happens only with minuscule probability, the single-excitation subspace is essentially only subject to the unitary dynamics according to the system Hamiltonian, excitation-number-conserving environment influences such as decoherence, and (excitation-number-non-conserving) relaxation to the ground state. Therefore, the single-excitation subspace evolves largely independently from the other subspaces even in the presence of decay mechanisms; and in particular, it does not significantly gain excitations from higher-lying states during the transfer through the complex. Excitation transfer can occur only via the excited states, since only then is an excitation (at least one) present. The transfer efficiency is usually evaluated by an observable, which is therefore defined only in the excited-state manifold, and, for the scenarios considered here, gains its dominant contribution from the transport dynamics of the single-excitation manifold. Contributions from higher-excited states constitute only a perturbative correction to the quantum state and therefore also to the observable that quantifies the transport properties. Common examples for measures of the transport efficiency are obtained by integrating the population of a certain exit site, e.g. decay to the reaction centre, as done in the study of Caruso *et al.* [5], or by the highest population of an exit site during a certain time window as in Scholak *et al.* [11], for example.

Formally, for an observable T that measures the excitation transport efficiency in the way described, and for initial states with only a small or even vanishing fraction of higher-excited states, one has

$$\langle T \rangle \approx \langle P_1 T P_1 \rangle, \quad (6.1)$$

that is, one can restrict the evaluation of T with good agreement to the predominant contribution from the single-excitation manifold, because higher-excited states yield only a perturbative correction to this result. Since the Hamiltonian conserves the number of excitation quanta, it is a valid approach to restrict the propagation of the entire excitation dynamics to the single-excitation subspace right from the beginning, as used in the last step of the following transformation:

$$\langle T \rangle \approx \langle \psi(t) | P_1 T P_1 | \psi(t) \rangle \quad (6.2)$$

$$= \langle \psi(0) | U^\dagger(t) P_1 T P_1 U(t) | \psi(0) \rangle \quad (6.3)$$

$$= \langle \psi(0) | P_1 U^\dagger(t) T U(t) P_1 | \psi(0) \rangle. \quad (6.4)$$

Because the projection to the single-excitation manifold is effectively carried out when measuring the transport efficiency, the projection may as well be exchanged with the dynamics to the beginning of the process.

Even with respect to open system dynamics, which is captured by the dynamical map $\mathcal{A}(t)$, that is, the map that contains the formal solution to the Liouville equation $\dot{\rho}(t) = \mathcal{L}\rho(t)$, one can approximate the transport efficiency by only considering the single-excitation manifold and the ground state:

$$\langle T \rangle = \text{Tr}[T\rho(t)] = \text{Tr}[T\mathcal{A}(t)\rho(0)] \approx \text{Tr}[T\mathcal{A}(t)P_{0,1}\rho(0)P_{0,1}]. \quad (6.5)$$

Regarding the evaluation of a measure of transport efficiency, it is thus, for the given assumption of weak light intensity, a natural and justified assumption to restrict the investigation to the subspace to only a single excitation.

In contrast to observables like measures of transport efficiencies, entanglement must be a *nonlinear* property of quantum states, and it can thus generally not be equivalent to coherences, which can be extracted by a linear operator. Because of these intrinsic properties of entanglement measures, it is not possible to exchange in a similar way the dynamics in the full space with a part that is projected to the single-excitation subspace. In fact, it is the projection to a subspace of fixed excitation number, which is a global operation, that introduces the observed entanglement into the system in the first place. In the present case of two molecules, the projection P_1 acts like a Bell-state measurement.

From the presented case, we can now provide an insight about whether or not the entanglement that may be observed in manifolds of fixed excitation number is of relevance to the state evolution or the transport properties of the system. The transport efficiency is robust under changes of the underlying models and assumptions about the initial state regarding the presence of small perturbative corrections of higher-lying excited states, whereas entanglement is not. Therefore, in a pigment–protein complex where an initial excitation merely evolves according to the system Hamiltonian and under a coupling to a bath, which introduces decoherence or relaxation, entanglement cannot be a quantifier of transfer efficiency. It cannot be the cause of a large transport efficiency, nor enhance the transport efficiency. The propagation of an excitation in a pigment–protein complex is different from the case of, say, quantum information communication tasks like quantum teleportation, where entanglement can be identified as the key resource and unentangled (separable) states cannot be used or, as another example, the fact that in interacting quantum systems entanglement is required to reach the ground state.

To conclude, in the first place, it is not at all clear to us that entanglement exists in the FMO complex; in fact, it seems to us that it does not. Entanglement, as it is at present postulated, relies on the existence of a single excitation in the FMO complex (technically a single-excitation Fock state). As we argued, this cannot be obtained by simply having very weak light impinging on the light-harvesting complex, as wrongly assumed in most literature on the subject. Consequently, if not simply due to low-intensity light, the only other way in which the postulated entanglement may still exist is if there were a dynamical, active, mechanism of state preparation. We argue that this is also extremely unlikely. Indeed, one would need a non-trivial process based on measuring the number of excitations, and opening the entrance of the FMO complex depending on the presence of a

single excitation. Crucially, this process should also eliminate the large vacuum component. Finally, and more significantly, even if entanglement exists, its role for the transport efficiency seems to us to be irrelevant, whereas the role of coherence may be important.

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