Does coherence enhance transport in photosynthesis?

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Recent observations of coherence in photosynthetic complexes have led to the question of whether quantum effects can occur in vivo, not under femtosecond laser pulses but in incoherent sunlight and at steady state, and, if so, whether the coherence explains the high exciton transfer efficiency. We distinguish several types of coherence and show that although some photosynthetic pathways are partially coherent processes, photosynthesis in nature proceeds through stationary states. This distinction allows us to rule out several mechanisms of transport enhancement in sunlight. In particular, although they are crucial for understanding exciton transport, neither wavelike motion nor microscopic coherence, on their own, enhance the efficiency. By contrast, two partially coherent mechanisms—ENAQT and supertransfer—can enhance transport even in sunlight and thus constitute motifs for the optimisation of artificial sunlight harvesting. Finally, we clarify the importance of ultrafast spectroscopy in understanding incoherent processes.

I. COHERENCE IN PHOTOSYNTHESIS

Photosynthetic complexes consist of a number of (bacterio)chlorophyll molecules, also called chromophores or sites, held in place by a protein scaffold (see Fig. 1 and Table I). We find that although the states are static, the experiments have shown the process to be coherent.

Several mechanisms have been proposed by which coherence might enhance the efficiency of exciton transport, and we discuss them in Sec. IIB, ruling some out for photosynthesis in sunlight. For example, because sunlight excites the entire complex—and not individual sites—and because transport is through a steady state, there is no “wavelike transport” that might speed up the exciton transfer. Similarly, although individual microscopic realisations are more coherent than the ensemble average, the microscopic coherences do not increase the efficiency. Indeed, in Sec. IIC we argue that coherence may be an evolutionary spandrel in most cases, as it is quite likely that equally efficient incoherent transport mechanisms are possible.

Nevertheless, we also identify mechanisms that can enhance transport. These mechanisms—ENAQT (Sec. IIB) and supertransfer (Sec. IIC)—constitute viable design principles for the engineering of artificial light-harvesting complexes.

Our findings do not imply that the oscillatory spectroscopic signals with coherent light are irrelevant; quite the opposite, coherent optical spectroscopy is indispensable for elucidating transfer mechanisms and providing evidence of the strong interchromophoric coupling that can lead to ENAQT and supertransfer in nature.

A. State and process coherence

A quantum state, described by a density matrix $\rho$, is called “pure” if it can be represented by a wavefunction, $\rho = |\psi\rangle \langle \psi|$, and “mixed” otherwise. The purity $\text{Tr}(\rho^2)$ is a basis-independent measure of how close a state is to being pure. Off-diagonal elements of $\rho$ are usually called “coherences,” but they are basis-dependent: a state diagonal in one orthonormal basis will not be diagonal in any other. Two bases are particularly important in discussing excitonic systems. The site basis is the basis in which each exciton is localised on a particular site, while the energy or exciton basis is the eigenbasis of the system Hamiltonian. Because of the coupling between sites, the two bases usually do not coincide.
| Type                     | Definition                                              | Remarks                                                                 |
|-------------------------|---------------------------------------------------------|-------------------------------------------------------------------------|
| Optical coherence       | Temporal correlation of the light field.                | The coherence of the incident radiation affects the molecular states that are created. |
| State coherence         | Purity                                                  | Basis-independent.                                                      |
|                         | In a particular basis                                   | Basis-dependent. Coherence in energy basis required for isolated system to undergo non-trivial time evolution. Coherence in site basis indicates exciton delocalisation. |
|                         | Off-diagonal element of density matrix.                 | Basis-dependent.                                                         |
|                         | Basis-dependent.                                        | Basis-dependent.                                                         |
|                         | In unitary evolution, coherences are static (unchanging). | Basis-dependent.                                                         |
| Static and dynamical    | At equilibrium or steady state, coherences are static (unchanging). | Basis-dependent.                                                         |
| coherence               | They are dynamical otherwise.                           | Basis-dependent.                                                         |
| Microscopic and ensemble| Ensemble coherence is the expectation value of the energy-basis coherences of each realisation (whose coherences are microscopic). | Basis-independent. Describes how long an initially coherent state stays coherent. E.g., unitary evolution is coherent, Förster transfer is incoherent. Importantly, a process can be coherent even if, in particular cases, it proceeds through steady states (as in photosynthesis). |
| Process coherence       | An open system evolves incoherently if the dissipation dominates unitary evolution and partially coherently otherwise. | Basis-independent. Describes how long an initially coherent state stays coherent. E.g., unitary evolution is coherent, Förster transfer is incoherent. Importantly, a process can be coherent even if, in particular cases, it proceeds through steady states (as in photosynthesis). |

Table I: Types of coherence discussed in this work.

Processes can also be described as coherent or incoherent. The evolution of an open quantum system consists of a unitary part and a dissipative part and the degree of process coherence depends on their relative strengths [17]. For example, an isolated system evolving unitarily is said to be evolving coherently, while Förster transfer is incoherent because the donor and acceptor are each more strongly coupled to their own dissipative environments than they are to each other, meaning that the slow transport between them will proceed at a simple rate [17].

The distinction between state and process coherence is important. Although long-lived state coherence implies partial process coherence, the converse need not hold: a process can be coherent even if, in particular cases, it proceeds through mixed states and can be described by rate laws. The fact that the system would evolve in a wavelike fashion if it were excited in the right way shows that the process itself is coherent even if particular realisations are not. That is, the coherent couplings are stronger than the noise even if that can’t be seen with, say, an initially mixed state.

**B. Excitation by lasers and by sunlight**

Until recently, most biological processes were thought to occur in an environment so warm and wet that the dissipative term would dominate the unitary term. The oscillations observed in coherent spectroscopic experiments [1–5] indicate that this need not be so. Femtosecond laser pulses can create non-stationary states—states with coherences in the energy basis—and the fact that these coherences persist for a long time is evidence of partial process coherence. A substantial debate exists about the extent to which these coherences are electronic or vibrational [18–20], but that distinction is beyond the scope of this work: we will consider them as coherences between the vibronic eigenstates of the complete molecular Hamiltonian.

While experiments have shown instances of photosynthetic light harvesting to be partially coherent processes, to understand whether photosynthesis involves coherent states in sunlight as well as under laser pulses, we must consider optical coherence. Light can be coherent in different ways, with various degrees of temporal, spectral, spatial, and polarisational coherence [21]. Spatial coherence can be assumed because photosynthetic complexes are much smaller than visible wavelengths, while polarisation coherence has little influence because of ensemble orientational averaging. The two types of coherence that are more important are the (related) temporal and spectral coherences. Classical light is “coherent” if its phase can be predicted at all times, and “partially coherent” otherwise. Sunlight is essentially incoherent because for black-body radiation at 5870 K, the coherence time is about 0.6 fs, shorter than other relevant timescales. Light
can be described in a fully quantised manner or semiclassically; the latter generally suffices for biological problems.

The coherence of the light absorbed by a molecule affects the resulting molecular state \([11 \, 22 \, 23]\), even if a single photon is absorbed \([24]\). The effect is most dramatic for isolated molecules: while coherent light can excite coherences in the energy basis, an ensemble of isolated molecules with non-degenerate levels, excited by incoherent light, will be in a mixture of energy eigenstates \([23 \, 24]\). Essentially, each non-degenerate transition will be driven by a different frequency component in the light, and these will have uncorrelated phases because the light is incoherent. When the random phases are averaged, the coherences disappear whereas the populations do not. Short pulses can excite coherences \([23]\), but because sunlight intensity is constant on light-harvesting timescales, these “turn-on” effects are of no concern.

The behaviour is slightly different for open systems. Since the result for isolated systems can be immediately applied to the system and the bath as a whole, coherences between system-bath eigenstates must vanish in the same way. However, upon tracing out the bath, energy-basis coherences of the reduced system may be substantial and may even approach the populations in magnitude \([11]\). A recent calculation of coherence dynamics in a multichromophoric system embedded in a structured, non-Markovian environment, found the coherences to be minimal \([25]\).

Importantly, natural light harvesting occurs at steady state, because the complexes are illuminated by weak sunlight whose intensity is constant at all relevant timescales. The complex is essentially a heat engine connected to two baths, the radiation at 5870 K and the cooler surroundings, which extracts work while steadily transmitting energy from the radiation to the surroundings. Therefore, whatever coherences remain in the system after tracing out the bath will also be stationary, up to negligible turn-on transients; that is, their phase will not evolve as \(e^{-i\omega_{ij}t}\) as it would if the system were isolated. In particular, this means that excitation by sunlight will not be followed by excitonic wave-like motion. Large stationary coherences can occur if the detuning between two levels is small and their relaxation fast, meaning that they are close in energy and broadened enough to make their spectral envelopes indistinguishable \([11]\). Indeed, tuneable systems could be arranged so that the static state coherence between nearly degenerate levels enhances the power from a photovoltaic cell \([20 \, 27]\).

### C. Absence of localised excitation

Although much can be learned about transport by considering an exciton initially localised on a particular site \([29 \, 30]\), the picture changes when one models light absorption. The wavelength of visible light is much larger than the size of photosynthetic complexes, meaning that all the chromophores experience the same electric field. Consequently, the steady state that is reached reflects the fact that the incoming radiation excites collective eigenstates of the whole complex, not individual sites.

The Fenna-Matthews-Olson complex (FMO) \([16]\) has been modelled with the excitation starting on sites that are believed to be closest to the chlorosome antenna that actually harvests the light \([29 \, 35]\). This approach should be adapted for studying light harvesting in sunlight: a chlorosome is as much an incoherent source of excitation as sunlight is. The energy transfer time from chlorosome to FMO (more than 120 ps \([37]\)) is much larger than the chlorosome’s dephasing time, meaning that the transfer is by an incoherent Förster mechanism. That is, the chlorosome excites FMO in much the same way as incoherent light does (Sec. 4.3 of \([11]\)). Even if site 1 were the only site coupled to the chlorosome, the chlorosome wouldn’t coherently excite site 1, to be followed by wave-like transport; rather, it would excite a mixture of FMO eigenstates in proportion in which they are found on site 1.

### D. Microscopic coherence

Studies of photosynthetic complexes have usually considered ensembles. In fact, each photosynthetic organism contains an ensemble of photosynthetic complexes, each of which experiences a slightly different environment (inhomogeneous disorder) \([9 \, 10]\). To properly understand natural light harvesting, it will be important to carry out single-molecule spectroscopic experiments to discern the mechanistic details that may be washed out in the ensemble average \([10 \, 38 \, 39]\).

An intriguing question is whether the state coherences of individual ensemble realisations—the microscopic coherences—play a role. Certainly, the ensemble density matrix, being the average of the microscopic density matrices, will have smaller coherences than the average absolute value of the microscopic coherences. Even if photosynthesis in vivo proceeded through diagonal steady states, the microscopic coherences might be non-zero. It is tempting to think that the potentially large microscopic coherences might affect light harvesting, by, for example, increasing its efficiency. For example, if each realisation used state coherence to enhance the efficiency, one would have to calculate the efficiency for each realisation and then average over the ensemble.

Having to simulate every realisation would be a Herculean task, but is fortunately unnecessary. Changing the order of ensemble averaging and calculating the expectation values of observables—including the efficiency
Figure 1: Photosynthesis in incoherent light, illustrated with a simplified model of LHII and LHI complexes from purple bacteria [16].

- a. Sunlight: incoherent, stationary
- b. An inaccurate picture: No light pulses, No localised excitation, No wavelike transport, Microscopic coherence doesn’t help
- c. A more accurate picture: Incoherent excitation Enhanced by supertransfer

η—makes no difference:

\[
\text{Tr} (\eta \langle \rho_S \rangle_{\text{ens}}) = \langle \text{Tr} (\eta \rho_S) \rangle_{\text{ens}},
\]

where \(\langle \cdot \rangle_{\text{ens}}\) is the average over realisations \(\rho_S\). Although some elements of the ensemble might benefit from state coherence, the benefit will be compensated in others. For example, if we imagine that the efficiency is proportional to a coherence, \(\eta \propto \rho_{12}\), then \(\langle \eta \rangle_{\text{ens}} \propto \langle \rho_{12} \rangle_{\text{ens}} = 0\) if the ensemble is diagonal. Although it is tempting to speculate about the efficiency including terms like \(|\rho_{12}|^2\), whose average would not vanish, it should be remembered that \(|\rho_{12}|^2\) is not a linear operator on \(\rho\) and therefore not a valid observable. Likewise, the purity \(\text{Tr} (\rho^2)\) is not an observable, so there is no contradiction if an ensemble of pure states has a purity less than 1. Non-linear expressions such as these are not observables because they cannot be measured in a single-shot measurement. Determining their expectation values is possible, but it requires the experimental ability to produce multiple copies of the same quantum state, which is not the situation in a genuinely random ensemble. Additionally, we do not claim that quantum systems can only respond linearly to external perturbations, but only that expectation values of observables are linear in \(\rho\) even if the response is nonlinear in the perturbation.

A similar situation occurs if one considers sunlight as a train of femtosecond pulses [7], in which case there is an ensemble of the phases and arrival times of these pulses. Even if each pulse could excite non-stationary states like a femtosecond laser could, the simpler, incoherent ensemble average will reproduce all the observables.

We do not seek to undermine the usefulness of single-molecule experiments, which are indispensable in elucidating biological mechanisms—as patch-clamping was for ion channels. We merely stress that once the mechanism is known, the outcome of a process can be calculated either microscopically or using the ensemble average, indicating that microscopic coherences do not play an important role in sunlight harvesting.

II. EXCITON TRANSPORT EFFICIENCY

Because the process of light-harvesting is partially coherent, it is tantalising to wonder whether the coherence might enhance the efficiency of exciton transport, suggesting it was selected by natural selection. The efficiency can be defined as the proportion of the initially created excitons that reach the reaction centre. Several mechanisms have been proposed by which coherence might enhance transport efficiency, and we consider how each of them might operate in the steady-state regime of natural light harvesting. We have already seen, in Sec. [II.D] that microscopic coherence cannot enhance efficiency, and in Sec. [II.A] we rule out another mechanism. Nevertheless, two mechanisms may be said to operate: ENAQT and supertransfer, discussed in Sec. [II.B] and [II.C] respectively. This is not to say that coherence is necessary for
highly efficient transport—indeed we argue that natural coherence may be an evolutionary spandrel and that although ENAQT and supertransfer may enhance the efficiency of artificial light-harvesting complexes, the possibility of efficient incoherent transport should not be overlooked.

A. Faster delocalisation

The simplest example of a difference between quantum and classical transport occurs on ordered, infinite lattices. On a one-dimensional lattice, quantum transport is “ballistic” because the variance of the particle’s wavefunction is proportional to time, $\Delta x_{\text{quant}} = c_{\text{quant}} t$. Classical transport, say by random walk, is “diffusive”, $\Delta x_{\text{class}} = c_{\text{class}} \sqrt{t}$. Therefore, at sufficiently long times, $\Delta x_{\text{quant}}$ will exceed $\Delta x_{\text{class}}$, even if $c_{\text{class}} > c_{\text{quant}}$.

If an excitation were initially localised, coherent delocalisation might enhance transport to a distant reaction centre. But as we noted above, photosynthetic complexes are much smaller than the wavelength of light, meaning that initial excitations are not localised. Furthermore, in any finite system, a classical particle could spread over the entire complex faster than a quantum particle if $c_{\text{class}}$ were sufficiently large. Therefore, even if an exciton in a biological complex initially spread ballistically, incoherent transport could cause faster delocalisation if the incoherent transfer rates were higher. In other words, the coherent speed-up of delocalisation cannot be said to be responsible for the high transport efficiency.

B. ENAQT

Environment-assisted quantum transport (ENAQT) can occur in systems whose evolution can be modified from coherent to incoherent using an adjustable coupling to a particular bath. ENAQT occurs if the efficiency of transport from one site to another is highest in the intermediate coupling regime, i.e., higher than it would be in either the unitary or incoherent limits. Although previous work has considered initially localised excitations, the steady state version is easily constructed as well.

In disordered systems, initially localised excitations may be prevented from delocalising by coherent effects such as Anderson localisation. ENAQT occurs if moderate decoherence destroys the coherent localisation, allowing the particle to reach its target. Similarly, very strong decoherence can prevent transport, meaning that adding partial coherence can optimise the efficiency. The extent of ENAQT is very dependent on the nature of the particular bath being studied. For certain realistic baths, the transport efficiency in FMO has been found to be optimised in an intermediate coupling regime; therefore, that complex can be said to have enhanced transport over the hypothetical case of weaker or stronger bath coupling. However, as we argue in Sec. IID, this does not show that coherence is necessary for the high efficiency.

C. Supertransfer

The second design motif is supertransfer, an enhancement of long-range incoherent transport by short-range process coherence. Named after superradiance, it involves a donor complex and an acceptor complex, each composed of several chromophores. The two complexes are far apart and the weak transfer between them incoherent (Förster), but the total incoherent rate depends on the process coherence within the donor. In the complete absence of process coherence, each chromophore in the donor is independently incoherently coupled to each chromophore in the acceptor by the dipole-dipole interaction. In the alternative case, the excitons within the donor are delocalised across multiple sites, allowing for cooperative transfer and an enhanced overall incoherent rate. In excitonic systems this effect is also known as multi-chromophoric Förster resonant energy transfer.

In the extreme case, incoherent transfer of excitons symmetrically delocalised across $M$ chromophores on the donor can be up to $M$ times faster than if the chromophores only communicated individually (see also the renormalisation scheme in (40)). For example, we consider a donor and an acceptor, each composed of two chromophores, all of whose dipole moments are parallel and with magnitude $\mu$. In the incoherent case, each chromophore in the donor has a $\gamma$ chance of being occupied and transmits to each acceptor chromophore with a Fermi-golden-rule rate $\gamma \sim |\mu_D \mu_A|^2 = \mu^4$. This gives a total incoherent rate of $\Gamma_{\text{incoh}} = 2\gamma$. If local coherence is present and the donor is in the symmetric ground state with dipole $(\mu_1 + \mu_2)/\sqrt{2}$ that communicates with the corresponding state on the acceptor, the total incoherent rate is doubled:

$$\Gamma_{\text{coh}} \sim \left( \frac{\mu_1 + \mu_2}{\sqrt{2}} \right)_D \left( \frac{\mu_1 + \mu_2}{\sqrt{2}} \right)_A = 4\mu^4 = 2\Gamma_{\text{incoh}}.$$

(2)

Supertransfer persists in incoherent light and at steady state, meaning that biomolecular networks in which supertransfer occurs, such as the LHI and LHII complexes in Fig. 1, may be said to have enhanced efficiency compared to the situation where all the chromophores were individually coupled.
D. Is coherence a spandrel?

ENAQT and supertransfer are both robust effects that may be used to explain the high transport efficiency in some complexes and that may be used in the design of artificial complexes. However, we must caution against the conclusions that process coherence always assists transport or that it is necessary for high transport efficiencies. Indeed, for any particularly efficient coherent process, one could increase the efficiency by adding additional incoherent rates direct to the reaction centre. Therefore, in engineering artificial light-harvesting systems, one should not consider process coherence necessarily advantageous.

This is not to say that there are no design motifs to be learned from photosynthesis: in certain artificial systems, ENAQT and supertransfer may be of great use.

The same caution should be applied to hypotheses that coherence is responsible for the high efficiency of photosynthetic exciton transport or that it was favoured by natural selection. Even if, for a particular bath, ENAQT calculations show that moderate coherence helps, we should recognise that evolution was not constrained to any particular bath (i.e., protein cage) and that a different bath could have yielded a more efficient, albeit incoherent, process. For this reason, we suspect that the observed process coherence may be an evolutionary spandrel\(^\text{[13]}\). It could well be that in trying to increase incoherent couplings and create an energy funnel to the reaction centre, evolution brought the chromophores closer, making strong interchromophoric couplings—and thus partial process coherence—unavoidable.

III. CONCLUSIONS

Although natural light harvesting proceeds through stationary states, long-lived dynamical coherences in ultrafast experiments remain remarkable because they show that the couplings between the chromophores are stronger than their couplings to their respective baths, which can indicate ENAQT or supertransfer even under incoherent illumination. Therefore, this artificial phenomenon is relevant not because it occurs in the same way \textit{in vivo}, but because it may indicate energy transport mechanisms that are qualitatively different from the previously assumed incoherent site-to-site hopping. Because this is the case if the observed dynamical coherences are of electronic and not vibrational nature, additional studies should address the origin of the oscillations\(^\text{[19, 20]}\).

A remaining challenge is to construct models of energy transfer under incoherent light based on spectroscopic data acquired with coherent light sources. Quantum process tomography helps achieve this goal by systematically correlating the prepared input and measured output states in the excitonic system\(^\text{[17, 18]}\). A complete characterisation may permit the control of energy flow using coherent light in the spirit of quantum control\(^\text{[20]}\), in which case dynamical coherences would be essential to achieving the desired goal.

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