"Light and life" – 88 years after

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"Light and life" – 88 years after. Quantum coherence in photosynthesis.

Introduction

88 years ago, Niels Bohr gave a lecture in Copenhagen called "Light and Life" (1), where he briefly addressed the connections between fundamental physics and biology. I believe that this topic is at the core of the discussion surrounding quantum technologies nowadays, as understanding how nature uses quantum phenomena could potentially shed some light on how we could use those same phenomena more efficiently for our quantum technologies.

One of the most well-studied and still controversial topics in this new field of quantum biology is quantum coherence in photosynthesis. Quantum computers rely heavily on quantum coherences of their "qubits" (quantum equivalent of bits of information) (2). These coherences can be thought of as information stability. Quantum decoherence, on the other hand, is related to information loss because of interactions of these qubits with the environment (3). To produce these quantum coherences, conditions such as near absolute zero temperatures are recreated, and even then, these coherences are extremely short-lived (2). Environments with ambient temperatures and no isolation from the surroundings are therefore, at least in principle, inadequate for these quantum coherences to appear (4). However, many studies have reported on the observation of long-lived quantum coherences in photosynthesis (5–10). These coherences are said to account for the near-unity quantum efficiency of the energy transfer in photosynthesis (10).

In this article, we will discuss if indeed quantum coherence takes place in photosynthesis and, if so, what is its role in the process. The reader will gain knowledge about how energy transfer in photosynthetic organisms works, with special emphasis on the explanation behind its surprising quantum yield.

Photosynthesis: the process

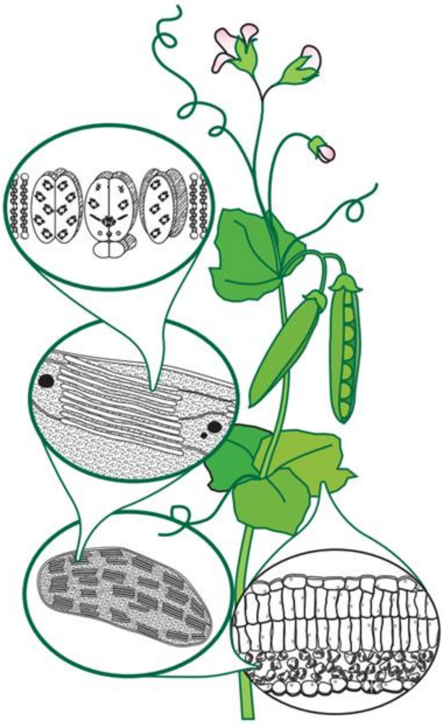

Fig. 1 Taken from ref. (11). The first bubble displays the cross-section of a leaf. The second one, a chloroplast. The third one zooms in the thylakoid membranes, and the final one shows the reaction centre surrounded by photosynthetic antenna structures. (Figure courtesy of Aileen Taguchi) (11).

First, we will delve into some specifics of the photosynthetic process such as its different phases and the main molecular complexes involved.

Figure 1 displays the different photosynthetic structures in eukaryotic cells. The energy-transfer mechanisms which we are concerned about occur in the thylakoid membranes, which are formed by a reaction centre surrounded by light-harvesting antennas (12). Both the reaction centre and the antennas are composed by chlorophyll molecules (chromophores) (6). The chlorophyll molecules which are further away from the reaction centre are high-frequency absorbing pigments, while the ones closer to it are low-frequency absorbing (11).

As pointed out by R.E. Blankenship (11), there are four phases in photosynthesis: a) photon absorption and energy delivery by antenna complexes, b) electron transfer in reaction centres, c) energy stabilization by secondary processes, and d) synthesis of final products. Our focus will be on the first phase.

When a photon reaches a leaf, light-gathering antenna absorb it creating an excited state in one chlorophyll molecule (6). The energy of this excited state is passed onto lower-frequency absorbing neighbouring chromophores until it reaches the reaction centre, which acts as a trap for this excitation energy (11). Once it reaches the reaction centre, an electron is released, and a pair of separated charges is produced. In this way, photosynthesis simply takes light energy and converts it into chemical energy which can be used by the organism (11).

So, where does quantum coherence come into play? The efficiency of this energy transport chain is near unity, which means that for almost every photon that is absorbed, an electron is produced by the reaction centre (11). This efficiency hasn't been fully explained by traditional models, which has led many scientists to believe that quantum coherent waves could play a crucial role because of their ability to take multiple paths at once (4).

Energy-transfer in photosynthetic antenna

The common model which is used to explain this energy transport is the Förster resonance energy transfer (FRET). This mechanism involves an excited chlorophyll molecule (the donor) which might transfer non-radiative energy to an acceptor chlorophyll molecule if the separation between them is around 1-10 nm and if both are coupled (13). Specifically, FRET occurs via dipole-dipole coupling (14). The first chlorophyll molecule has an excess energy because of the photon it has absorbed. As a result of this, an emission photon is created by this donor molecule, and, because of the dipole interactions between the two molecules, the photon is absorbed by the acceptor before the photon actually takes on physical significance (non-radiative) (14).

A direct consequence of this is what's called "surface hopping" of the excitation energy (11). According to FRET, the excitation energy "hops" from one chromophore to another, following a downhill energy flow until it is finally trapped in the reaction centre, which is the lowest energy state (15–17). This downhill energy flow appears because of the disposition of the chromophores illustrated by Figure 2.

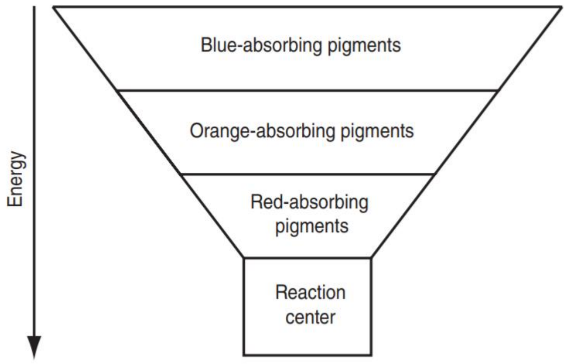

Fig. 2 Taken from ref. (11). Energy flow diagram of the excitation energy from the photosynthetic antenna to the reaction centre (11).

FRET is intrinsically quantum-mechanical, as it follows Fermi's golden rule (18). This rule establishes the probability of transitions of an energy eigenstate to a group of energy eigenstates, such as the transition of the energy states of the chromophores (19). The strength of the coupling between the initial and final states will determine how high that probability is (19). Nevertheless, quantum coherence does not play a role in FRET, and the quantum mechanics outlined above are trivial for this discussion in the sense that there is no quantum "weirdness" which accounts for the high efficiency of photosynthesis.

The main problem of the FRET model is that it only works for weakly coupled molecules (11). If the chlorophyll molecules are closer than ~1 nm, other energy transfer processes not described by this model may occur (6). The average inter-chromophore distance is 0.6 to 2.5 nanometres, so, even though FRET does provide some insights on photosynthetic energy transfers, complementary models which take into account stronger molecular interactions are needed (6).

Before we go on to the other energy transfer models, it is necessary to explain what quantum coherence is exactly.

Quantum coherence

Coherence is a synonym of a fixed phase relationship between two waves (20). The first thing to note is that coherence is not an exclusive phenomenon of the quantum world. For instance, it can be observed in the oscillatory motion of two coupled pendulums. Quantum coherence is purely observed in the superposition of quantum eigenstates of a system. This can be visualized with Young's double-slit experiment.

In the quantum world, every particle can be represented by a wavefunction. So, when we shoot an electron through two-slits, instead of just going through one slit like a normal macroscopic ball, its wavefunction splits into two states (eigenstates). These states interfere with each other, forming a wavelike interference pattern at the detector instead of just creating two uniform incidence patterns.

It is extremely complicated to reproduce quantum coherences because of the interferences of the system's wavefunction with the environment's wavefunction. These interferences lead to a loss of some quantum properties of the system. In light of this, we will be using the definition provided by J. Cao *et al* in their 2020 paper "Quantum biology revisited", which states that quantum coherence in photosynthetic energy transfers is a measure of the degree to which the state of the chlorophyll molecules corresponds to a linear superposition of different eigenstates of the system (21).

There are different types of quantum coherences in terms of their physical origin: vibrational, electronic or vibronic (22,23). Vibrational coherence derives from molecular vibrations, while electronic coherence involves the charges (electrons) of the molecules (22). The vibronic coherence is simply a mix of the last two which happens when molecular vibrations are coupled to the electronic states of the molecule (23).

When molecular systems are electronically excited (by a photon, for instance), quantum coherent waves which are delocalized appear (23). Because of interactions of these waves with the environment, the waves can effectively disappear, and the excitation becomes localized (21,23). These two types of excitations, localized and delocalized, are called incoherent and coherent excitons respectively (23). Coherent excitons are just another name for electronic coherences in the energy eigenstates of the molecules.

Quantum coherence in photosynthetic energy transfers

The complementary model that we were searching for before is exciton propagation. The question at hand now is whether these excitons propagate coherently or incoherently through the photosynthetic antenna. This is the big question of this discussion. Are plants capable of maintaining long-lived electronic coherences in hot, noisy environments to attain high-efficiency energy transports?

Vibrational coherences don't have a direct influence in photosynthetic energy transfers (unless coupled to excitons) because the excitation energy is electronic in nature, not vibrational (18). The relevant types of coherence for this discussion are therefore the electronic and vibronic ones.

As we have seen, quantum coherences in a system like a chloroplast should be extremely short-lived because of the lack of isolation from environmental influences. The predicted lifetime of these coherences is around 100 fs (18,24,25), but several studies have reported electronic or vibronic coherences of 660 fs and longer in recent years (5–10). They explain that the delocalization of the excitons due to their coherence allows energy to take multiple paths through the coherent clusters of chromophores at the same time, making the process more efficient. Simulations of this coherent energy transfer have shown that it is 3.3 times faster than incoherent energy transfers (22).

However, more recently, many scientific papers have been published which have explained that the supposedly long-lived electronic coherences observed were, in fact, vibrational in origin (21,24,25). To understand their analysis, we will look into 2D electronic spectroscopy (2DES), the experimental method which has been used to gather these data.

Two-dimensional electronic spectroscopy

2DES is a spectroscopy technique which reveals vibrational, electronic and vibronic coherences in a system (26). Quantum beats are produced over a range of frequencies (detection frequencies) by exciting the system with a laser (excitation frequencies) (5,26). The laser must have a spectrum broad enough to include all the quantum

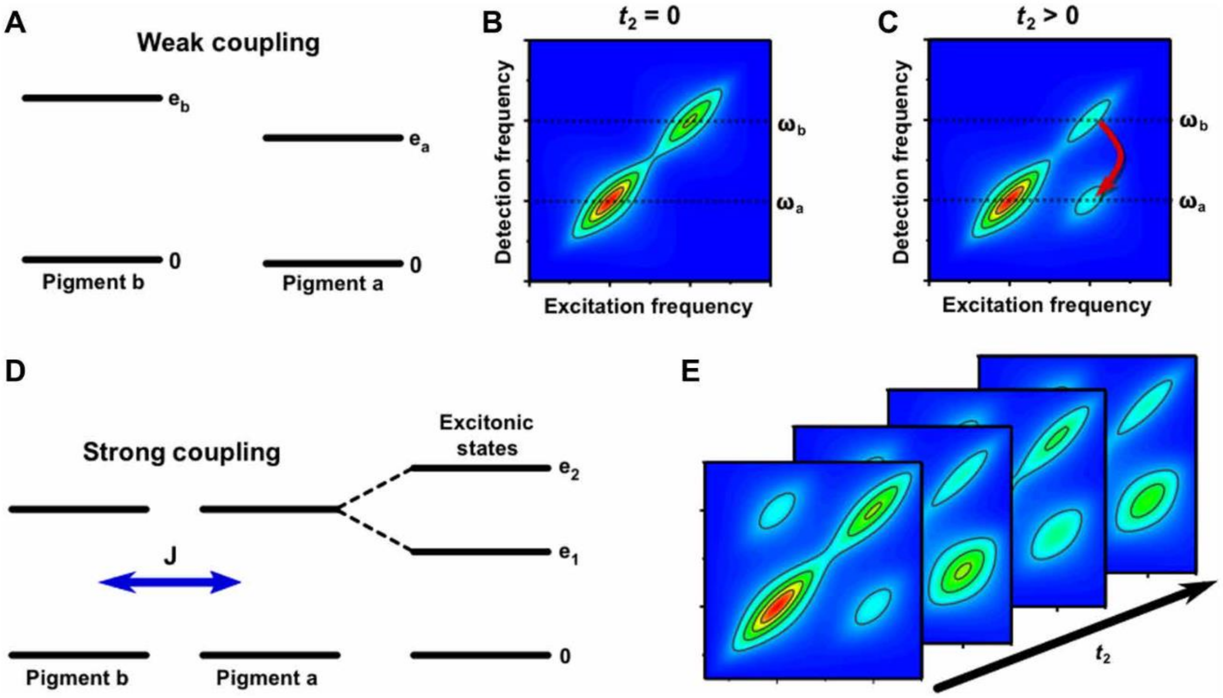

Fig. 3 Taken from ref. (21) A) Schematic of the energy eigenstates e_a and e_b of two weakly coupled chlorophyll molecules a and b. B) 2D absorption spectrum showing two peaks along the diagonal representing the absorption (detection) frequencies ω_a and ω_b of each chromophore. C) After some time, an energy transfer (FRET) from the higher-energy one (b) to the lower-energy one (a) might occur. This energy transfer can be seen in the appearance of a cross-peak (red arrow). D) Simple schematic of the coherent excitonic state created by the superposition of the energy eigenstates of two strongly coupled chromophores. E) This mixing of the energy eigenstates can be observed at t=0 in the form of two cross-peaks. As time increases, oscillations (increasing and decreasing intensity) can be observed at this cross-peaks, revealing electronic quantum coherence (21).

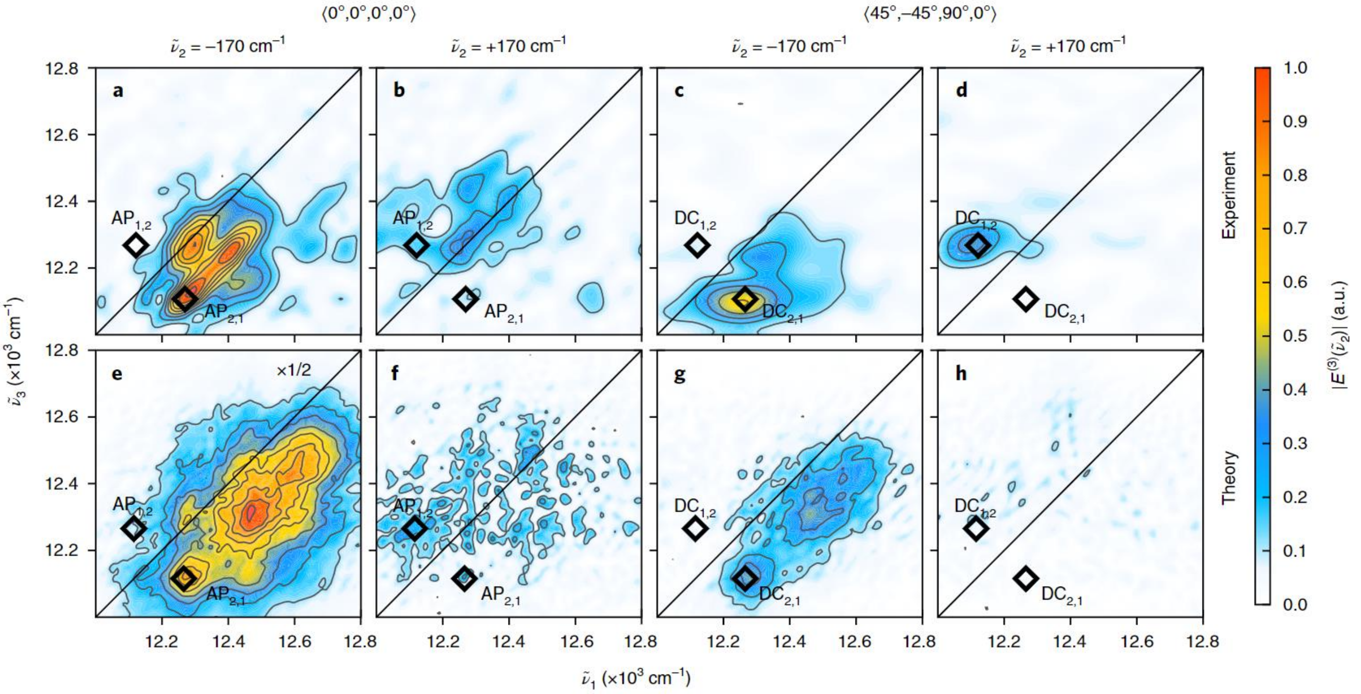

Fig. 4 Taken from ref. (24). Graphs from (a) to (d) show experimental 2D spectra, while (e) to (h) show theoretical predictions using simulations. All of them represent the quantum beats (areas in black squares) of the exciton found at $\pm 170\ \mathrm{cm}^{-1}$ in the FMO complex at 77 K. The ones on the left half (a,b,e,f,) show the spectra obtained using an "all parallel" polarized laser pulse (AP), while the ones on the right half (c,d,g,h) show the spectra of a "double crossed" polarised laser pulse (DC). Using lasers with different polarisations might reveal different couplings of the system, as it is the case here. The AP laser reveals vibrational coherence, while the DC graphs manifest vibronic coherence (24).

beat frequencies of the system in order to be able to detect them (21). Furthermore, the laser pulses must occur in shorter timescales than the period of the quantum beats (21). Figure 3 shows how to interpret a 2D spectrum.

Figure 4 shows the 2D spectra obtained from a bacteriochlorophyll complex (FMO) at 77 K. As outlined by several research groups (24,27,28), 2D spectra with cross-peaks which are diagonally symmetric reveal electronic coherence. Cross-peaks which are diagonally asymmetric and whose features in the negative detection frequency are stronger than in the positive detection frequency correspond to vibrational coherences. Finally, cross-peaks which are also diagonally asymmetric, but which have similar intensities in their positive and negative 2D spectra, refer to vibronic coherences. In light of this, we can see in Figure 4 that the cross-peaks which were said to be long-lived electronic coherences in the FMO complex (graphs A and B) are, in fact, vibrational coherences (21,24,25).

Apart from the vibrational coherence, vibronic coherence has also been observed using a laser pulse with different polarisation (DC), which suggests that, even though there is no long-lived electronic coherence, short-lived vibronic coherence might play a role in photosynthetic energy transfer, but this is still unclear (18,24).

Noise-assisted energy transport

One last point needs to be made before we conclude. Even though interactions with the environment will in principle lead to nothing more than energy dissipation and all sorts of negative effects, it has been demonstrated that, actually, noise can increase transport efficiency (29,30).

Different chromophores have different energies. If their coupling is weaker than the energy gap between them, energy transfers won't take place (29). Environmental noise can help by shifting the energies of the chromophores, making it possible for them to overcome the energy difference (29,30). This phenomenon has been reported to increase efficiencies of 70% up to 99% (29).

Conclusion

In order to explain the incredible near-unity efficiency of energy transfers in photosynthesis, we have seen three different models. All of them are intrinsically quantum mechanical, but only the second one argues that long-lived quantum coherences are the main reason behind the high efficiency of those transfers.

The first one involves Förster resonance energy transfer (FRET), which states that excitations in the chromophores are transmitted towards the reaction centre through surface hopping and following a downhill energy flow (11). However, this model isn't able to explain energy transfers in antenna fully because it only applies to weakly coupled chromophores (11).

Both the second and third models involve exciton propagation, but in different ways. The second one asserts that this exciton propagation is quantum coherent and, consequently, delocalized, while the third one affirms that the propagation is mostly incoherent, with environmental noise assisting the energy transfer (23,29). The delocalization implied by the second model would allow the excitons to propagate through multiple pathways at once, making the process more than three times faster (22).

However, it has been shown that the experimental observations which supported the view of a coherent exciton propagation revealed vibrational coherences and not electronic coherences (21,24,25). As the transmitted excitation energy is not vibrational, these coherences don't have a direct influence in the energy transfer (24).

Noise-assisted energy transport is able to account for the high efficiency of the process (29). Nevertheless, relevant vibronic coherences which were not predicted by simulations have been found in photosynthetic organisms, suggesting that they aid exciton propagation in some way (24). Further studies will have to study this phenomenon in more detail.

Whichever the correct model is, a proper understanding of this process could be an inflexion point in the development of new quantum technologies such as organic photovoltaics and quantum computers (6,18). Photovoltaics are already benefitting from concepts such as noise-assisted energy transfers, and the field of quantum computing could be revolutionised if ideas on how to use coherences at ambient temperatures are incorporated to the new designs (18).

Even though there is still much to be said about this highly controversial topic, a mix of the first and third models has been suggested by many as the most promising viewpoint (11). FRET explains energy transfers between weakly coupled molecules, while noise-assisted energy transport with vibronic coherences can account for strongly coupled interactions (11). The main idea to take home, however, is the complexity of photosynthesis and the realisation of how finely tuned it is to reduce energy losses in complicated environments. With the era of quantum technologies upon us, there is definitely much to be learned from this little light trap.

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