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Mini Review

Is Photosynthesis Quantumish or Not So Quantamish?

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Abstract

Nature itself is a huge laboratory with plants on it as an experimental setup, performing the incredible process of photosynthesis. Photosynthesis, as a process, has been extensively studied and as such, all the mechanisms occurring therein are well known from the biochemical point of view. However, the study of the phenomenon from a quantum perspective is quite new. There is growing evidence that quantum coherence plays a role in photosynthesis, however, the fact is not clear to that level of accuracy. Therefore, a better understanding of this process is both interesting and fruitful.

Keywords: Photosynthesis; Quantum coherence; Efficiency; Reaction center

Introduction

Photosynthesis, the biological process whereby solar energy is stored as a fuel, is the vital link between the energy of the Sun and life on Earth. During the early steps of photosynthesis, light-harvesting complexes absorb and transfer solar excitation energy to the Reaction Centre (RC), the site of energy conversion. In the RC the excitation energy is converted into a transmembrane electrochemical potential with near-unity quantum efficiency, that is, almost every absorbed photon is converted into a charge-separated state. Despite the present knowledge about the pathways and timescales of charge separation, the precise mechanism responsible for the high efficiency of this process is unknown. The quantum coherence between the electronic states involved in energy or electron transfer introduces correlations between the wave functions of these states enabling the excitation to move rapidly and to coherently sample multiple pathways in space. Therefore, the quantum coherence effect may render the process of energy and electron transfer less Sensitive to the intrinsic disorder of pigment-protein complexes and allow these systems to successfully reach their final state avoiding energy losses. Two-dimensional electronic spectra 2DES reveals the presence of coherent effects in photosynthetic complexes. According to specific realizations of Redfield model, the disordered excition-CT model is used to generate the dynamics of the site populations of the cofactors' excited states and the primary CT state for specific realizations of the disorder to investigate the effect of coherence on charge separation. We can conclude that the correlation between electronic coherence and the speed and efficiency of charge separation strongly supports the idea that electronic coherence plays a major role in determining the speed and efficiency of the first charge-separation step. The combination of experimental and theoretical evidence provides a link between the presence of quantum coherence and its biological functional role in the PSIIRC.

According to the disordered exciton-CT model, which captures the 2D spectral shape and overall time evolution very well, we may conclude that vibration-assisted electronic (vibronic) coherence is present in the PSII RC and, as indicated by the relative quantum-beat amplitude, it exists in a large fraction of PSII RCs. Furthermore, the correlation between electronic coherence and efficiency indicates that vibronic coherence is used by the system to drive ultrafast and efficient charge separation. Therefore, in line with recent theoretical work, the vibronic coherences survive the aggressive background noise and consequently may play an essential role in charge separation dynamics. Based on the substantial evidence, we may propose that the PSII RC has evolved a delicately tuned and robust environment to provide the required exciton-vibrational matching for efficient solar-energy conversion and, consequently, that the plant PSII RC operates as a quantum-designed light trap.

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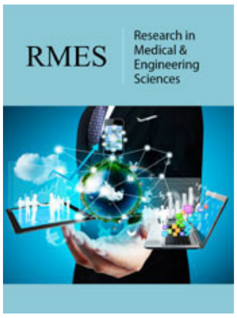

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However, there is more to the story. During the first steps of photosynthesis, the energy of impinging solar photons is transformed into electronic excitation energy of the light-harvesting bio-molecular complexes. The subsequent energy transfer to the reaction center is commonly rationalized in terms of excitons moving on a grid of biomolecular chromophores on typical timescales <100fs. Today's understanding of the energy transfer includes the fact that the excitons are delocalized over a few neighboring sites, but the role of quantum coherence is considered as irrelevant for the transfer dynamics because it typically decays within a few tens of femtoseconds. This conventional picture of incoherent energy transfer between clusters of a few pigments sharing delocalized excitons has been challenged by ultrafast optical spectroscopy experiments with the Fenna-Matthews-Olson protein, in which interference oscillatory signals up to 1.5ps were reported and interpreted as direct evidence of exceptionally long-lived electronic quantum coherence. The optical 2D photon echo spectra of this complex at ambient temperature in aqueous solution do not provide evidence of any long-lived electronic quantum coherence. Our results can be considered as basic and give no hint that electronic quantum coherence plays any bio-functional role in real photoactive bio-molecular complexes. The conditions under which matter displays quantum features or biological functionality are contrarious. Quantum coherent features only become apparent when systems with a few degrees of freedom with a preserved quantum mechanical phase relation of a wave function are well protected from environmental fluctuations that otherwise lead to rapid de-phasing. This de-phasing mechanism is very efficient at ambient temperatures, at which biological systems operate. Also, the function of biological macromolecular systems relies on their embedding in a "wet" and highly polar solvent environment, which is again hostile to any quantum coherence [1-6].

The common view of multichromophoric Forster resonance energy transfer has been developed in which excitons are quantum-mechanically delocalized over a few neighboring pigments, but a quantum coherent phase relation between the clusters involved in any biologically relevant dynamical process is rapidly destroyed on a sub-100-fs timescale. The transport is dominated by dipolar coupling between the sites with different energies, such that it is spatially directed and naturally leads to energy relaxation and flow to the reaction center. The nature of any quantum coherence is short-lived and could, at most, only involve a few neighboring sites-a views that is typically different from that of a large quantum coherent process as implied by very long-lived electronic coherence living as long as proposed. Advanced dynamical simulations did not confirm long-lived electronic coherence and, as a consequence, wave-like energy transfer. An additional strong coupling of the excitonic to the nuclear degrees of freedom was also considered as a possible driving source of coherence. Such a mechanism can yield longer-lived oscillations of the cross-peak amplitude, yet, a strong vibronic coupling is required, and the oscillation amplitudes typically remain small. Within the available experimental signal-to-noise ratio, we can conclude that there are no oscillations with amplitudes >5% of the signal. They may be interpreted as weak vibrational coherence, steady with earlier findings for a much smaller excitonically coupled system (a dimer) with strong vibronic coupling. The new work provides a full analysis and thus shows that the previous assignment of weak long-lived oscillatory signals in 2D spectra to long-lived electronic coherence is incorrect. There is no long-range coherent energy transport occurring in the FMO complex and, in all cases, is not needed to explain the overall efficiency of energy transfer. The contributions of quantum coherence to biological functionality under ambient conditions in natural light-harvesting units is extremely unlikely, a finding being in line with the previous study of the light-harvesting complex LHCII.

Conclusion

Both the ideas have been presented and there is an equal likeliness that photosynthesis may be quantamish or it may not be so, however, more research needs to be done to arrive at more robust conclusions so that this phenomenon can be exploited to meet the energy needs by designing processes artificially which are analogous to natural photosynthesis. This is a rich field. Insightful experiments have reinvigorated energy transfer research. The resulting accelerated development of theories has been breath-taking. The stage is set for young researchers to solve the new challenges now in sight.

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