Decoherence in Photosynthetic Energy Transfer

Abstract

In efforts to better understand the light harvesting mechanisms of photosynthetic organisms, several studies, both experimental and theoretical, have examined hypotheses related to the role of quantum coherence in the energy transfer process between chromophores (e.g. chlorophyll) en route to the photosynthetic reaction center.

Researchers have sought to answer several questions: does quantum coherence play a role in Photosynthetic Energy Transfer (PET)? If so, do the results of low temperature experiments with coherent laser light apply to the ambient temperatures of environments where such organisms are exposed to incoherent sunlight? If yes, how crucial is it to the speed and efficiency of the process? Is it sufficiently long-lived to play a non-trivial role in the optimization of these processes? If so, was it directly evolutionarily selected for? Can knowledge of these mechanisms be co-opted for technological developments?

Although experiments have been conducted measuring oscillatory patterns in the spectroscopic signals of photosynthetic complexes, there has been considerable disagreement among biophysicists on how these data should be interpreted. Here, I present a brief outline of the ideas, experiments, concepts, and arguments under discussion, and summarize the picture that has been gradually emerging from the growing body of scientific literature on this topic.

Introduction

The notion that quantum mechanical effects might play non-trivial roles in biological systems has been conjectured as far back as the late 1920s, shortly after the foundations of quantum theory were first laid down.[1] Pioneers of the field such as Niels Bohr and Erwin Schrödinger both expounded upon the question, the latter of whom purportedly influenced Watson and Crick, co-discoverers of the DNA double-helix, to investigate the nature of genes.[18, 2, 3, 1] Moreover, as early as 1938, Franck and Teller proposed a PET model in which they considered the diffusion of a *Frenkel exciton*, a coherent superposition of electronic excitations of pigment molecules.[4, 5]

However, only within the last 15-20 years has the study of *quantum biology* begun to attract significant attention, and this has raised questions regarding its future potential as a scientific subdiscipline. Of course, there is no serious debate over whether the atoms and molecules comprising organisms are governed by the same underlying physics as everything else. But, there are questions regarding the extent to which distinctly quantum effects in biological subsystems are of sufficient magnitude and duration (compared to the strength their interactions with their environment) to play a functionally relevant role, and whether invoking the language of quantum mechanics meaningfully enhances our understanding of them. Indeed, one of the central ideas underlying the concept of decoherence in many-body systems has been that classical behavior is an *emergent property* of intrinsically quantum systems interacting with an environment, which then *washes away* the coherence.[6] So, even if some element of a biological system could be prepared in an initial coherent state, how long until its coupling to multiple degrees of freedom in its environment causes it to decohere into a statistical mixture?

An even bigger question is whether distinctly quantum effects have been directly evolutionarily selected for. It would be one thing to show that coherence, tunneling (or even entanglement) can be detected in biological systems. That could just as well be an incidental trait which came along for the ride via circumstantial association with more distinctly adaptive ones. But the discovery that any kind of *quantum-optimized* process conferred a fitness advantage of any kind would go a long way in solidifying quantum biology's standing as a necessary scientific subdiscipline.

One topic on which researchers have sought to answer such questions is the study of energy transfer mechanisms in photosynthesis. While evolution has produced a variety of light-harvesting complexes (LHCs), it has done so while utilizing a comparatively small number of pigment molecules which absorb photons and generate electronic excitations (excitons), whose propagation enables the organism to convert the energy of photons into usable chemical energy.[7]

Perhaps the most iconic model of oxygenic photosynthesis is the Z-scheme, an energy level diagram according to which thylakoid membranes of chloroplasts contain protein complexes called photosystems I and II, an antenna complex consisting of an arrangement of pigments, and a cytochrome complex.[8] Recent investigations into the role of coherence in photosynthesis have been concerned only with the initial steps of this process: the excitation of electrons in pigment molecules in the antenna complex upon absorption of photons, and resonance energy transfer between nearby chromophores en route to a part of photosystem II called the reaction center.

The early research purported to challenge the conventional view of this process as a semi-classical "hopping" mechanism, by which the excitation energy is transferred in a step-wise fashion down an energy gradient from one exciton state to the next, dissipating energy at each step, analogously to a drunkard staggering downhill.[20]

Theory:

Energy transfer in networks of chromophores is often described by semi-classical models based on Förster resonance theory.[9] In such models, a donor molecule is excited by a photon specific to its fluorescent excitation wavelength, the energy of which is then non-radiatively transferred to a neighboring acceptor molecule via a local dipole-dipole coupling mechanism.[10] Concurrently, the donor molecule returns to its pre-excited state. This occurs within the spectral overlap of the emission and absorption spectra of the donor and acceptor respectively, and with an efficiency that is inversely proportional to the 6th power of the distance between the adjacent chromophores. This is famously expressed by the Förster equation: $E = \frac{1}{1+(\frac{r}{R_0})^6}$, where E represents efficiency (quantum yield), r represents the distance between adjacent chromophores, and R_0 is the Förster distance, defined as the distance at which the transfer is 50% efficient, and which depends on the yield of the donor, the spectral overlap between donor and acceptor, the refractive index of the medium, and a factor associated with their directional orientation in space.[11, 9] This then proceeds as a sequence of energy transfers between members of an array arranged such that the emission spectrum of each donor overlaps with the absorption spectrum of a nearby acceptor.

Although this is often implemented as an incoherent hopping of excitons between energy levels, some semi-classical, stochastic, and quantum-classical generalizations have been developed at varying levels of approximation, some of which include coherent effects.[12] For example, the Redfield equation describes the time evolution of the density operator ρ of a quantum system that is weakly coupled to its environment.[12] In this approach, the total Hamiltonian is broken into $H = H_{\text{sys}} + H_{\text{env}} + H_{\text{int}}$, corresponding to the system of interest, the environment, and an interaction term, each of whose elements must be inferred from experimental data. If interactions between the system and environment are weak, H_{int} can be treated as a perturbation. If the Hamiltonian can be diagonalized (even if only numerically), a complete set of exciton states can be obtained. In this exciton basis, the time evolution of a density matrix can then be obtained by taking its commutator with the Hamiltonian: $\dot{\rho}(\mathrm{t}) = -\frac{i}{\hbar}[H, \rho(\mathrm{t})]$.[19] Although originally developed for NMR spectroscopy, this approach and modifications thereof are often used in quantum biology.

Experiment:

Perhaps the study which most conspicuously influenced the subsequent influx of interest in this topic was Engel et al 2007.[13] This team used 2D Fourier Transform Electronic Spectroscopy to build upon previous research which had already mapped the electronic energy levels and their coupling in the Fenna-Matthew-Olson (FMO) bacteriochlorophyll complex. The FMO is a pigment protein complex (PPC) comprising part of the photosynthetic apparatus mediating energy transfer in green sulfur bacteria (chlorobium tepidum, in this case). Compared to many other known PPCs, FMO’s structure and optical properties are relatively simple and well-understood, thus it is a common object of study in a variety of research applications.

In the case of Engel et al 2007, three short light pulses and a strongly attenuated local oscillator were incident upon the sample, which was kept cold at a temperature of 77 K. The spectrum of the light pulses spanned multiple known exciton transition wavelengths, and the pulse durations were typically on the order of tens of femtoseconds. The first of these pulses was to generate a coherence which would evolve for a time τ, the second of which was to generate an excited state population that would evolve for a time T, and the third of which was to generate another coherent state which would accumulate an oppositely directed phase for a time t, after which a rephasing would occur coincident with the emission of a signal pulse. The electric field of said signal pulse was measured using spectral interferometry. In short, the first pulse would induce coherent excitons, and the following would probe for signs of quantum beats.

The goal here was to probe electronic excitations and couplings and energy transfer in the FMO complex by mapping the way in which excitations prior to time T would affect the subsequent emission after time t. The reasoning was that off-diagonal peaks signify couplings between electronic energy levels, because in the absence of such coupling, excited state absorptions and emissions would cancel each other out, leaving no evidence of off diagonal elements. In contrast, if long-lived coherences were indeed occurring, it was expected that beating signals should emerge in the shapes and amplitudes of the resulting peaks whose frequencies would correspond to the energy differences between individual exciton states. If this were to be observed, they reasoned, these “cross-peaks” would seem to suggest a phase difference, which would indicate the presence of non-zero off-diagonal terms, and therefore imply a superposition of excitation states: a quintessential signature of coherence.

That's exactly what Engel's team found: quantum beats whose duration exceeded earlier model predictions, lasting for over 660 fs. Or at least, so they thought. They conjectured that this might imply the evolution of a *quantum search*, whereby excitons sample many paths simultaneously and converge with higher probability on the most efficient one than for alternatives.

Various subsequent studies were published seeking to follow up on this work, and disagreements arose over the interpretation of the data measured by Engel and others. One of the more definitive of these in recent years was Miller et al 2017.[14] By this time, the initial question had bifurcated into multiple related debates. For example, the importance of distinguishing between superpositions of electronic excited states vs the concurrence of multiple characteristic vibration frequencies in a population (electronic vs vibronic coherence) was recognized as relevant to interpreting the signals Engel's team and others had interpreted as electronic coherence.

On the one hand, Jonas et al 2012 argued that the observed beats were attributable to molecular vibrations due to Raman scattering, rather than true electronic coherences, and that vibrational wavepacket motion on the electronic ground state would likely outlive any electronic or coupled vibrational-electronic coherences and would thus play a larger role in PET.[15,] That would be consistent with the orthodox semi-classical view. In contrast, Plenio et al 2013 proposed that long-lived vibrationally coherent modes could actually enhance electronic coherence lifetimes when the electronic and vibronic degrees of freedom are resonantly coupled.[16]

Miller's team sought to address some of these issues in 2017. It was a combined experimental and theoretical study which sought to test the FMO complex long-lived coherence in what the authors argued were more biologically relevant conditions, since they were done at 296 K, which is much closer to the temperatures of the aquatic and terrestrial environments most photosynthetic organisms inhabit than the temperatures at which the earlier work was performed.

Their experimental setup involved ultrashort coherent laser light pulses using a broadband spectrum with a FWHM of 100 nm centered on a 770 nm wavelength and a pulse duration of 16 femtoseconds. The team used optical 2D photon echo spectroscopy to record and analyze electronic dephasing and vibrational coupling in the FMO protein complex. They also subtracted out the slow kinetics from the 3D data set to make it easier to distinguish the signatures of coherent electronic and vibronic oscillatory signatures respectively. Essentially, the crux of their argument was as follows: According to their models, all the exciton states in the FMO complex were confined to the range of 12,123 - 12,615 cm^{-1}.[14] Therefore, the largest oscillation frequency that could plausibly be expected from the beatings between them should be about 490 cm^{-1}. Yet, the lowest oscillation frequency they found was well above 600 cm^{-1}. Therefore, they reasoned, the observed oscillations could not have originated from interference between exciton states.

They went further by performing a cross-correlational analysis, from which they note two negative peaks which they argue are characteristic of localized vibrational coherence according to criteria established in previous studies for distinguishing between electronic vs vibronic coherences. They concluded that these match the frequency, amplitude and decay rates of known Raman vibration signatures, and that this strongly supports the orthodox view that electronic coherences in FMO decay rapidly (on the order of 60 fs), and thus any meaningful contributions of electronic coherence to PET efficiency are highly unlikely. Rather than *beating* decoherence, they argued that photosynthesis achieves the efficiency it does by *exploiting* it.[20] They also claim that this finding is likely general, and applicable to larger photoactive biomolecular complexes.

Outlook:

What I've presented here is a mere snapshot of just a few of the studies examining this topic. Most of these researchers have done studies on multiple distinct but related ideas, as have other scientists not mentioned here. The full story of this debate is beyond the scope of this treatment.

That said, although disagreement among researchers in this area clearly still exists, the current preponderance of evidence suggests that any role played by electronic quantum coherence in PET is likely negligible. Yes, it shows that it's possible to co-opt the language and mathematical formalism of quantum mechanics to model biological systems, but at least in this case, the utility and explanatory power of doing so appears to be limited (at least in hindsight). The goal is not to merely shoehorn theoretical frameworks where they're not needed just because they've been successful in another context. The goal is to better understand the world. And presently, the stochastic semi-classical picture of decoherent excitons hopping stepwise between allowed energy states seems an adequate model of how this energy transfer occurs.

Although this is just one narrow area of investigation, it has broader relevance in the context of establishing the importance of quantum biology as an emerging scientific discipline. Some proponents have alluded to quantum-optimized biological processes as a possible design principle of nature, and this research seeks to ascertain whether photosynthesis constitutes an example of this.[17] There are other candidates, and a quantum approach may still turn out to be necessary for maximal understanding of certain biological systems, but the current state of the research leans provisionally towards this not being one of them.

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