Overview of Possible Quantum Mechanics in Photosynthesis

Joseph S. Choi[1], Dr. John C. Howell[2]

[1]The Institute of Optics, University of Rochester; [2]The Department of Physics and Astronomy, University of Rochester, 14627

Introduction

Biological systems achieve near unity efficiency in solar energy conversion through photosynthesis. Quantum coherence may play a vital role in this process, increasing energy transfer speed and efficiency. Here, we provide a brief overview of some research in the field probing quantum mechanics in photosynthetic systems.

Research Review 1

Collini et al. reported evidence of quantum coherence in photosynthetic marine algae at ambient temperature (294K)[1]. The used two-dimensional photon echo spectroscopy to probe the light-harvesting antennae of two types of cryptophyte algae (only one is presented here).

These algae can photosynthesize in low-light conditions. They are particularly effective despite the comparatively larger distance than plant counterparts.

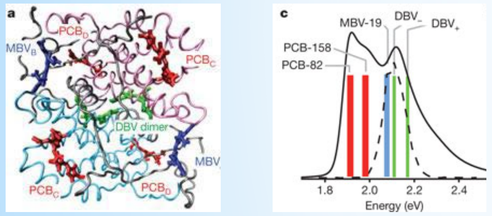

Figure 1: **a** Structural model of PC645, an algae protein with 8 light-harvesting molecules that form an "antenna." **c** Electronic absorption spectrum of PC645 in aqueous buffer (294 K).

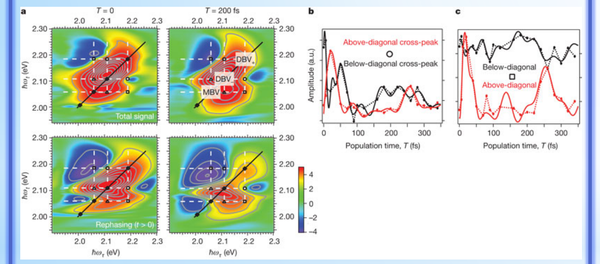

Figure 2: Two-dimensional Photon Echo data for PC645.
a Left column is for 0 waiting time (T = 0), with rephasing contribution (t > 0). Right column is for T = 200 fs, during which time the population density can evolve. Signal intensity is plotted vs. coherence frequency (ω_τ) and emission frequency (ω_t). **b** Intensity of the DBV dimer cross-peaks (open circle) as a function of time *T*. **c** Intensity of the MBV-DBV$_+$ cross-peaks (open square) as a function of time *T*.

- A coherent superposition of the antenna protein's electronic-vibrational eigenstates cause a coherent oscillation to be seen. In the experimental data, anti-correlated oscillations provide evidence that both DBV dimer and DBV-MBV electronic superposition states exist.
- The coherence persists for **> 400 fs** after photo-excitation, which is quite long, given the ambient temperature of the process.
- This coherence spans from the DBV dimer to the peripheral MBV molecules, over a distance of **25 Å**. This distance is about double that of typical light-harvesting protein in plants.
- The results suggest that quantum effects could facilitate the efficient light-harvesting by cryptophyte algae.

Methodology Review- 2D Photon Echo Spectroscopy

Two-dimensional Photon Echo (2DPE) Spectroscopy has been used widely and proved quite effective in probing coherence of photosynthetic molecules. Minhaeng Cho and Fleming's group have developed an intuitive approaches to explaining this technique[2, 3], so we present it here.

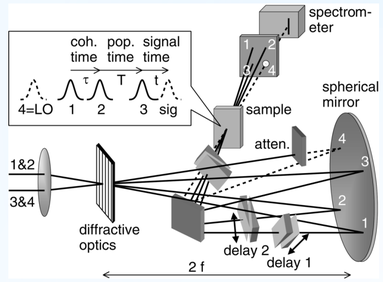

Figure 3: Experimental setup for frequency domain heterodyne detected 2DPE spectroscopy.
- A reference field (the "local oscillator") beats with signal field to preserve phase info.

$$\left| E_{sig}(\omega) + E_{LO}(\omega) * \exp\{-i\,\omega\,t_{LO}\} \right|^2$$

- 4 pulses are produced by diffractive optics. After delay wedges, they are recombined by the mirror.
- Momentum conservation ($k_s = -k_1 + k_2 + k_3$) allows separation of signals.

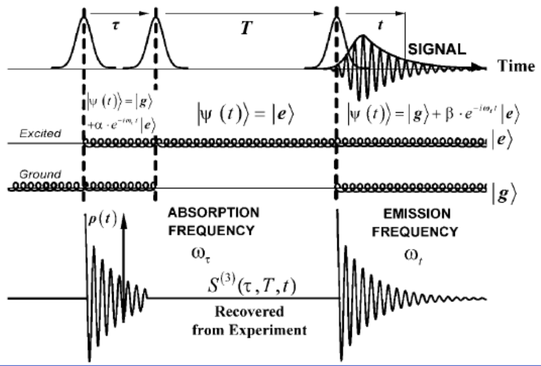

Figure 4: Sequence of events in a two-level system leading to photon echo.
1. First pulse leaves system in quantum-mechanical superposition of ground and excited states. The time, **τ**, is called the **Coherence Time**.
2. Second pulse converts superposition into a population (diagonal) state. **T** is called the **Population Time**.
3. Finally, third pulse converts population into superposition of the first, leading to echo generation during the period **t**, the **Signal Time**.
4. Signal, $S^{(3)}(\tau, T, t)$ is Fourier transformed into $S^{(3)}(\omega_\tau, T, \omega_t)$.

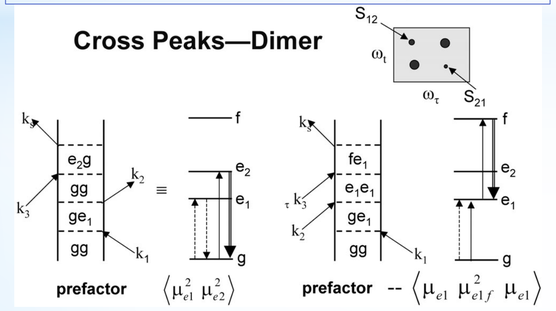

Figure 5: Origin of transition dipole terms controlling cross-peak amplitude for dimer.

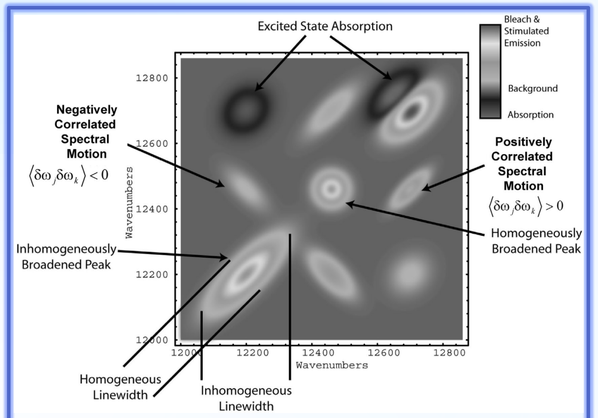

Figure 6: Schematic representation of a two-dimensional spectrum at fixed T.

- 2D spectrum is not symmetric around diagonal due to different transitions with differing dipole strengths that are involved (S_{12} vs. S_{21} in Fig. 5).
- Cross (off-diagonal) peaks appear (for T=0), only when coupling between chromophores is present. They can also be generated by energy transfer for larger values of T.
- The transition frequency cross correlation function, or the spatial overlap of the probability density functions of two exciton states, also determines cross-peak amplitudes and the rate of electronic relaxation energy transfer.

Research Review 2

Engel, et al., used two-dimensional Fourier transform electronic spectroscopy to probe the energy transfer pathway for the Fenna–Matthews–Olson (FMO) bacteriochlorophyll complex. This is found in green sulphur bacteria and acts as an energy 'wire' connecting a large peripheral light-harvesting antenna, the chlorosome, to the reaction centre, where the energy storage is initiated for this photosynthetic system. They found evidence for wavelike energy transfer due to quantum coherence[4].

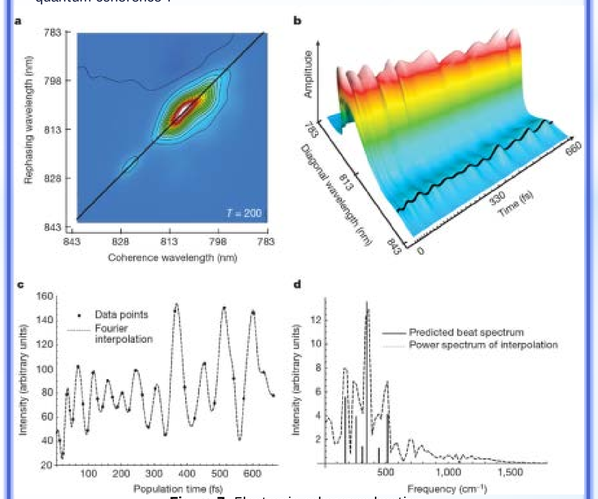

Figure 7: Electronic coherence beating.

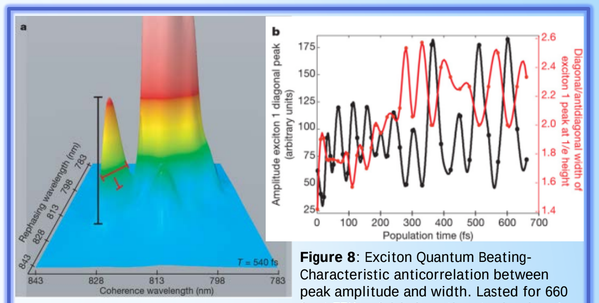

Figure 8: Exciton Quantum Beating-Characteristic anticorrelation between peak amplitude and width. Lasted for 660 fs at 77K, a fairly long time to decohere!

Research Review 3

Lee, et al., performed a 2-color photon echo experiment on a bacterial reaction center. Their data revealed long-lasting coherence between two electronic states that can only be explained by strong correlation between protein-induced fluctuations in the transition energy of neighboring chromophores. This suggests electronic coherence is preserved by correlated protein environments in photosynthetic complexes. Thus, they showed that the protein structure and long-range system-bath interactions are important for efficient photosynthesis[5].

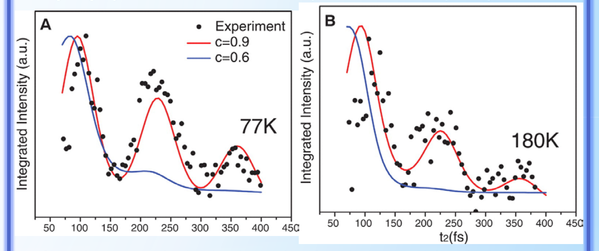

Figure 9: Integrated echo signals as a function of t_2 at t_1 = 30 fs. Plot is the dephasing dynamics of the |B><H| coherence.

Future

We plan on further elucidating how quantum mechanics, coherence, and possibly entanglement are used in photosynthesis. Through theoretical modeling, high-precision spectroscopic experiments, we hope to understand and engineer this capability in nature to make progress for an energy solution.

References

[1] Collini, E. *et al*. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. *Nature* **463**, 644-U669, (2010).

[2] Cho, M. H., Brixner, T., Stiopkin, I., Vaswani, H. & Fleming, G. R. Two dimensional electronic spectroscopy of molecular complexes. *Journal of the Chinese Chemical Society* **53**, 15-24 (2006).

[3] Brixner, T., Stiopkin, I. V. & Fleming, G. R. Tunable two-dimensional femtosecond spectroscopy. *Optics Letters* **29**, 884-886 (2004).

[4] Engel, G. S. *et al*. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature* **446**, 782-786, (2007).

[5] Lee, H., Cheng, Y. C. & Fleming, G. R. Coherence dynamics in photosynthesis: Protein protection of excitonic coherence. *Science* **316**, 1462-1465, (2007).

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Further Information

Please contact Joseph Choi: joschoi@optics.rochester.edu