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Report on the Ph.D. thesis of David Paleček (Quantum Coherence for Light Harvesting)

The doctoral dissertation thesis by David Paleček is extremely interesting scientifically. The thesis contains a well-written and accessible introduction to a body of work on the role of quantum mechanical coherence in photosynthetic light harvesting. Some results of the thesis have already been published in three papers in respected journals, but the thesis also contains additional manuscripts of even higher quality and originality. The thesis obviously merits the Ph.D. For reasons explained below, my opinion is that David Paleček's thesis belongs to the very rare group of Ph.D. theses that will be judged in hindsight to have pushed their field forward in a major way.

The introduction explains why coherence might be important for photosynthesis and also summarizes the current state of the field, which is in a state of scientific upheaval. Photosynthetic pigment complexes often have ordered crystal structures that have been resolved by X-ray crystallography. However, the field is challenging because the coupling strengths between pigments are usually unknown, there are complications from energetic disorder, the electronic excitations are coupled to a bath of intramolecular and protein vibrations, and the most efficient steps are always finished in less than a picosecond ( $10^{-12}$  s). The prime tool for investigating electronic dynamics in such complicated systems is femtosecond two-dimensional Fourier transform electronic spectroscopy, a technique that is still under active development 17 years after initial demonstration and still imperfectly understood for such complicated systems. The very basic questions at the heart of the field right now are: What kinds of coherence cause the oscillations in 2D spectra of photosynthetic complexes? and What role (if any) does each kind of coherence play in the energy transfer process? David Paleček's thesis contains original contributions to understanding both energy transfer and the most powerful technique used to study it.


As explained clearly in the introduction, the first published paper from the thesis contains a mis-step that was in line with thinking at the time (2012), yet this paper also emphasized the problem that electronic coherences could not out-live the superposed electronic states as they seemed to do. The resolution of this apparent paradox is the thread running through the rest of the thesis. This thread takes interesting turns through low temperature spectroscopy of self-assembled bacteriochlorophyll aggregates, 2D tests for vibronic coherence in a tubular aggregate of cyanine dyes, analysis of simpler nonlinear optical measurements related to polarized 2D spectroscopy, analysis of polarized 2D measurements, a 2D study of energy transfer in the oxidized photosynthetic reaction center of purple bacteria, comparative studies of different models for their 2D spectra, and studies in mutant reaction centers. The later chapters show a growing

sophistication in experiment, theoretical interpretation, and use of the feedback loop between them to improve our understanding of energy transfer in the oxidized bacterial reaction center and to resolve the paradox posed in the first paper.

The key to this thesis lies in the difficult and time consuming 2D experiments used to measure the 2D map of the oscillations previously observed when looking at peaks in 2D spectra as a function of the waiting time. For the oxidized bacterial reaction center, some of these 2D oscillation maps have the symmetry between cross-peaks expected for electronic coherence, yet oscillate for an order of magnitude longer than the population lifetime of the excited state. The 2013 paper by Tiwari et al. showing that strong purely vibrational coherences could be generated on the ground electronic state through a novel non-adiabatic coupling on the excited state was a clue, but did not solve the puzzle for the reaction center because the ground state vibrations generate an asymmetry between cross-peaks (a prediction consistent with the reported 2D spectra of some antennas). Tiwari et al. also pointed out that their excited state coupling mechanism predicts that excess energy can be left behind as vibrational excitation of the ground electronic state of the donor after energy transfer electronically excites the acceptor. This is referred to in manuscript paper IV as a shift of vibrational population during energy transfer. The major new insight of the thesis is to propose a corresponding shift of vibrational coherence during energy transfer. This is a mechanism for vibrational cross-peak oscillations to arise on the ground electronic state of the donor, and oscillations on the ground electronic state of the donor are practically required by the excited state population lifetime. The thesis then goes on to show that this energy transfer induced coherence can account for the symmetric oscillation amplitudes of the two cross-peaks and the time-varying phase of the cross-peak oscillations, which are carefully measured and calculated.

The greater information content of the 2D oscillation maps and their good agreement with the coherence shift signatures raises a host of interesting questions about the ubiquity of 2D oscillations arising from vibrational coherence transferred to the ground state of the donor vs. 2D vibrational oscillations generated on the ground electronic state by the optical pulses. I also see interesting questions about the role of excited state absorption in these signals. The careful combination of experiment and theory in this thesis is quite unusual in the field, which has a rapidly moving research forefront. In my opinion, the insights David Paleček has generated by this vital combination make for an especially praiseworthy Ph.D. dissertation.

Sincerely,



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