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Minireview

Photosynthetic exciton theory in the 1960s

Robert M. Pearlstein
Physics Department, Indiana University-Purdue University at Indianapolis, Indianapolis, IN 46202-3723, USA (e-mail: iebh100@iupui.edu; fax: +1-317-876-7557)

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Abstract

Theoretical developments in the 1960s concerning the migration of chlorophyll electronic excitation energy through a photosynthetic core antenna to a reaction center are reviewed in three parts. These include the first theory paper whose calculated results were consistent with experiment, the first analytic determination of the mean number of steps in the two-dimensional random walk of a dephased exciton to reach the reaction center, and the first theoretical description of the possible effects of true collective excited states (Frenkel excitons) on the rate of trap-limited migration and trapping. The possible relevance of these developments, particularly the last, to current photosynthesis research is briefly discussed.

Introduction

As the 1960s began, it had already been more than two decades since James Franck and Edward Teller (1938) had declared an exciton-transporting chlorophyll antenna in a photosynthetic organism to be an impossibility. This minireview briefly covers the period when Franck and Teller's gauntlet was first successfully taken up. I first describe the developments that led to the first published theory of the migration and trapping of chlorophyll excitation energy in photosynthesis that was consistent with available experimental findings. Following that, I review the events that led to the first analytic determination of how the mean number of steps in the two-dimensional random walk of a hopping exciton depends on the number of core-antenna chlorophylls per reaction center. Finally, I write about the first theoretical exploration of the speeding up (or slowing down!) of the rate of trap-limited excitation by true collective states, Frenkel excitons.

The making of Bay and Pearlstein

In the summer of 1962 three physicists – Zoltan Bay, John Avery, and I – gathered in the Woods Hole, Massachusetts, laboratory of Albert Szent-Györgyi. Our purpose was to try to extend the theoretical work published the previous year by Avery, Bay, and Szent-Györgyi (1961) on energy transfer in biological systems. This had become a recent interest of Szent-Györgyi, who, in the year I was born, had been awarded the Nobel Prize in medicine for his discoveries regarding vitamin C. Avery et al. (1961) had argued that, if the wave functions of the electronic excited states of a set of identical molecules within a biological system retained their relative phases over some period of time, the system might be able to take advantage of that to concentrate the excitation energy at some useful locus. As it turned out, we never did address this issue squarely that summer because we were diverted by the question of whether definite phase relations could be maintained long enough to produce an observable effect. This was, after all, 10 years before the first report of exciton lines in the spectra of antenna chlorophylls (Philipson and Sauer 1972).

Bay, on leave from the US National Bureau of Standards (now National Institute of Standards and Technology), and an old friend and colleague of Szent-Györgyi, led the group. Initially, Avery, then of the University of Chicago, was the theorist and I was the experimentalist. At that time, I was a teaching assistant in the Department of Physics and Astronomy at the University of Maryland, having just completed my second year of graduate studies there. At the beginning of those studies, I had worked for Bay at the National Bureau of Standards (NBS) and we had published an experimental physics paper together (Bay and Pearlstein 1963a).

For the first several weeks of that summer, the three of us met each morning in a room on an upper floor of the (now) oldest building of the Marine Biological Laboratory (MBL), where Szent-Györgyi's Institute for Muscle Research was housed. We would discuss progress and problems before going about our separate tasks. Thus, I became conversant with the project's theoretical issues. That proved a good thing because, when (for personal reasons) Avery left the project in mid-summer, I became the theorist!

By that time, our focus had pretty much narrowed from biological systems in general to photosynthetic units consisting of antenna plus reaction center, or bulk chlorophyll plus photochemical trap as they were then known, in photosynthetic organisms. By fortunate coincidence my old Harvard College classmate, Charles (Chuck) Weiss, Jr., was in Woods Hole that summer as assistant to James Franck. Chuck and I spent many hours plying the stacks of the MBL Library and attempting to educate one another on the latest research findings in photosynthesis. Thus I also became the photosynthesis 'expert' of the Szent-Györgyi group.

The Szent-Györgyi group eventually took the viewpoint that any thermally excited vibration within one of the identical molecules of the biological system would randomize the phase of that molecule's electronic excited state with respect to the excited states of the other molecules. This viewpoint might now be considered a bit extreme, though it still has qualitative merit. Initially, though, Bay was opposed to it because he thought that such dephasing was equivalent to a determination of the position of the electronic excitation, which, he argued, ought to require a loss of a significant portion of that energy (Bay and Pearlstein 1963b) – something that does not happen during excitation energy transfer between identical molecules. He accepted the idea – indeed enthusiastically embraced it – once we understood that dephasing and localization were not one and the same thing. That is, the absolute square of the wave function of the excitation could still be delocalized over the set of identical molecules even after any concentrating effect of phase coherence was lost. In modern parlance, one would say that the population elements of the exciton density matrix, which lie on the main diagonal of that matrix, may all remain nonzero, even after all the off-diagonal elements (which express the phase information) have decayed to their equilibrium values (Reineker 1982). For an introduction to the density matrix in quantum mechanics see, for example, Sakurai (1994).

The premier theory of excitation energy transfer between molecular electronic-transition dipoles given complete phase randomization (in the above sense), then as now, was that of Förster (1948). The question that Bay and I next confronted was how to apply Förster's theory to a photosynthetic unit. Our objective was to calculate the chlorophyll fluorescence lifetime as limited by the mean time for an excitation quantum to reach the photochemical trap, assuming that energy conversion at the trap was much faster than the process of energy migration through the antenna. Franck and Teller (1938), using a model one-dimensional structure (a linear chain of chlorophylls) with a Förster-like transfer mechanism, had found the migration to be too slow to be compatible with observed fluorescence yields. Bay and I suspected that the increased number of transfer pathways in a higher-dimensional structure would greatly speed up the process, so we decided to investigate two- and three-dimensional model structures. The reports of thylakoid structure in chloroplasts emerging about that time (Sauer and Calvin 1962; Park and Pon 1963) encouraged us to do so. Since so little was then known about antenna structural details, we wanted to make as few assumptions as possible about them in our calculations, which led us to try a diffusion model.

Förster's theory applied to energy migration involving more than two molecules, as in a photosynthetic antenna, can be expressed as a set of coupled first-order rate equations. As Förster himself had noted (Förster 1948), this set of equations could be approximately replaced by a single diffusion equation – a partial differential equation in which the discrete distribution of phase-randomized excited-state populations over the chlorophylls is approximated by a continuous distribution of excitation probabilities in the region of space encompassed by the antenna. However, to my knowledge, neither Förster nor anyone else

up to that point had *solved* the full three-dimensional diffusion equation for the process of excitation migration and trapping in any system where the bulk and trap sites are both distributed three-dimensionally. Setting up the problem in this way was what enabled Bay and Pearlstein to avoid Frank and Teller's unfortunate introduction into photosynthesis of one-dimensional kinetics, in which the diffusion-limited trapping time depends on N^2, where N is the number of bulk (antenna) chlorophylls per photochemical trap. Solving the problem required (1) determining the diffusion constant, (2) establishing boundary conditions, and then (3) actually solving the Sturm-Liouville problem of diffusion equation plus full three-dimensional boundary conditions.

Toward the end of the summer Bay returned to NBS in Washington and I, having agreed to stay on at MBL, was left alone to find the solution. A diffusion constant has dimensions of rate times area. At that time, I took it to be simply the product of the Förster rate constant for energy transfer between nearest-neighboring chlorophylls and the square of the distance between those chlorophylls. Later, in my doctoral thesis (Pearlstein 1966), I derived a more precise diffusion-constant expression for regular arrays of chlorophylls. Determining an appropriate boundary condition at the trap proved a greater challenge. Perhaps the greatest uncertainty was how large to set the radius of the trap. In a diffusion approximation to a discrete set of coupled rate equations such a radius was, in effect, an artifact. In 1962, I simply took it to be the nearest-neighbor chlorophyll separation. In my thesis, I gave more elaborate methods to estimate it. The ultimate solution, of course, was to solve the coupled rate equations directly – see the next section.

In Woods Hole that fall, I concentrated on solving the excitation-migration diffusion equation in a three-dimensional region of spherical symmetry. In part, that was because Bay and I believed it would give a faster migration (it did) and, in part, because it meant I could avoid dealing with the Bessel functions (for which I had no handy references at MBL), necessary for the analogous two-dimensional solution. (Of course, I had to deal squarely with those Bessel functions in my thesis – see below.) The diffusion solution consists of an infinite series of exponentially decaying terms, but in three dimensions 95% of the initial excitation decays with the lifetime of the first term in the series, labeled zero. Later I realized that this 'zero-mode dominance,' as I called it in my thesis, is the rule in any diffusion problem with a symmetrically placed sink (trap) and a uniform initial condition. At the time, though, it was exciting to realize that this strong zero-mode dominance meant that the migration and trapping could be characterized by a single lifetime (in a given photosystem). Moreover, that lifetime turned out to be compatible with what was then known of chlorophyll fluorescence lifetimes *in vivo* (Latimer et al. 1957; Tomita and Rabinowitch 1962; Butler and Norris 1963). Bay and Pearlstein's (1963c) calculated result was the first to provide a conceptual and theoretical understanding of the above experimental results.

In December 1962, I reported my findings to Bay face-to-face in Washington. He was clearly pleased. How pleased, I was only to learn when I later returned to Woods Hole after the holidays. Albert Szent-Györgyi sent word that he wanted to see me at his elegant home out on Penzance Point. I had only visited once or twice before and only in the company of Bay. Fearing the worst, I was ushered into the bedroom where the great man, having just turned 70, was propped up on his bed, his leg immobilized by a large cast (he had broken it in a skiing accident just a week earlier). Only then did I learn that Szent-Györgyi had summoned me to lavish praise, both Bay's and his, for my accomplishment.

The story of N log N

Bay and Pearlstein (1963c), though it broke new ground, was hardly error free. We had not, for example, faced squarely the then emerging concept of two photosystems in oxygenic photosynthesis (see Pearlstein 1964). We also were not right about the dependence of the migration-and-trapping lifetime on N, the number of antenna chlorophylls per photochemical trap. Getting the N-dependence right was one of my principal concerns as I worked on my thesis at the University of Maryland during the years 1964–1966.

In the fall of 1964, when I passed my PhD qualifying examination, my committee stated that my degree could not be awarded on the sole basis of the work I had done in Woods Hole, a ruling I had expected. The committee members recommended that I seek the direction of Elliott Montroll, then Research Professor in the Institute for Fluid Dynamics and Applied Mathematics at the University of Maryland, in completing my thesis. Knowing Montroll's reputation in statistical physics, including particularly random-walk

theory, I gladly followed this recommendation and was delighted when Montroll agreed to take me on.

Montroll was very busy and I saw him rarely. He pretty much let me direct myself, making an occasional suggestion when we did meet. My focus at that time was to develop the diffusion approximation into a reasonably accurate substitute for numerical solution of the set of coupled rate equations (also known as the master equation). Besides a desire to *know* the correct N-dependences of the migration-and-trapping lifetime (still assuming that photoconversion at the trap was essentially instantaneous) in two and three dimensional chlorophyll arrays, there was a practical consideration. In the mid-1960s, the only computers were mainframes, lumberingly slow by today's standards and very expensive to use. The cost of an hour's time, in dollars of those days, was almost as much as the purchase price of a modest personal computer in today's currency (moreover, today's PCs with suitable software can do such calculations in a fraction of the time). One could save significant funds given reliable analytic formulas for the lifetime in terms of N.

How was one to go about finding these analytic N-dependences? Before hooking up with Montroll, I had been able to run a number of numerical calculations on both two and three dimensional model arrays thanks to the generosity of the University of Maryland (Pearlstein 1964). For the three-dimensional arrays it was clear from the numerical results that as N increased the lifetime became proportional to N to a high degree of accuracy. But for two-dimensional arrays the numerical results showed that the ratio of the lifetime to N continued to increase without apparent bound as N increased. This was at odds with an earlier result calculated by ten Bosch and Ruijgrok (1963), which implied that the lifetime divided by N was bounded as N tends to infinity. Knox (1968), in what to my knowledge was his first published contribution to photosynthetic exciton theory, later showed that their result was flawed.

For me, the breakthrough came in early 1965 when I solved the excitation diffusion equation for an appropriate set of boundary conditions in two dimensions and from that solution (in terms of Bessel functions) derived the behavior of the lifetime for large N. I found that it was proportional to N log N, i.e. N multiplied by the logarithm of N. Montroll (1964) had almost derived this result the previous year in a different context, except that additional steps would have been required to make it germane to the photosynthetic antenna problem.

In 1966, when I was invited to present the results of my thesis work at the Nineteenth Brookhaven Symposium on Biology (Pearlstein 1967; see Figure 1 for a group photograph of that conference), I felt a certain pride of discovery regarding N log N, which I displayed for the first time to the photosynthesis community. At that meeting I met G. Wilse Robinson, who also presented an invited talk on excitation transfer and trapping in photosynthesis (Robinson 1967). During his talk, Robinson gave the results of some numerical calculations on random walks in square arrays intended to model the chlorophyll antennas of photosynthesis. These results were similar to those of my own numerical calculations of two years earlier (Pearlstein 1964), so I was pleased to see them. In his talk, Robinson made no mention of the dependence of the migration-and-trapping lifetime on N.

When the published version of the Symposium appeared in 1967, I saw that Robinson had fit his numerical calculations using my N log N dependence. Though his constant of proportionality differs from mine by only about 2%, mine is simply a three-significant-figure rounding off of a precise analytic result. If the logarithm is taken to base e (natural logarithm), that result, when expressed in terms of the mean number of steps in the random walk instead of the migration-and-trapping lifetime, is exactly the reciprocal of π. The same analytic result precisely was obtained later by Montroll (1969) when he re-derived the N log N dependence directly from random walk theory.

Concentrating effect of phase coherence

A year or so after the 1966 Brookhaven meeting, now as a member of the research staff at the Oak Ridge National Laboratory, I returned to energy transfer theory. In the summer of 1963 in Woods Hole, when I first met him, Rod Clayton had asked me what the migration-and-trapping lifetime would be if the excited-state wave functions were to maintain definite relative phases during the migration and trapping process. Another way to put this was what would be the kinetics of the process if the antenna chlorophyll Q_Y states were true collective excited states, i.e. Frenkel excitons? The idea was to put aside temporarily the dephasing lifetime issue that had so bemused Avery, Bay, and me in the summer of 1962. Instead, one should simply ask just how much the maintaining of precise phase relations could speed up the process over

Figure 1. Participants at the 1966 Brookhaven Symposium on photosynthesis (from left to right). *Back row:* W. Menke, G. W. Robinson, T. Punnett, J. Friend, R. P. Levine, H. T. Witt, R. E. McCarty, A. T. Jagendorf, N. E. Good, R. C. Fuller, G. Forti, B. Kok, D. L. Keister, and R. Bachofen. *Center row*: R. B. Park, P. Joliot, K. Sauer, S. Izawa, S. Miyachi, W. A. Arnold, T. E. Weier, L. N. M. Duysens, G. M. Cheniae, H. Linschitz, A. San Pietro, M. Nishimura, B. C. Mayne, W. W. Parson, W. J. Vredenberg, J. M. Olson, R. A. Dilley, and M. Schwartz. *Front row*: H. Lyman, R. K. Clayton, R. M. Pearlstein, E. I. Rabinowitch, Govindjee, D. C. Fork, M. Avron, M. Baltscheffsky, B. Chance, L. Packer, R. A. Olson, O. v. H. Owens, E. Gantt, B. Ke and G. Hind.

incoherent diffusion (or random hopping) of the excitation. I had been wondering about that ever since and finally took up the challenge.

First I had to define the problem more precisely. People had long been accustomed to equating the migration of a collective excited state – a Frenkel exciton – with great speed compared to that of a randomly hopping state. After all, the former involved directed wave motion while the latter was 'simply' diffusion. However, in my thesis I had already explored the issue of diffusion-limited *versus* trap-limited migration-and-trapping of diffusing excitation, and seen that the diffusion rate was high enough that transfer from the antenna into the trap itself might prove to be a bottleneck (Pearlstein 1966, 1967). It occurred to me then that transfer-to-trap would be even more of a bottleneck for the rapidly migrating exciton waves. Thus, one had better treat the two processes – exciton motion and transfer-to-trap – in coupled fashion. I devised a simple mathematical model in which to carry out such a coupled treatment (Pearlstein 1968, 1972).

My purpose here is not to review the mathematics of the coupled treatment itself, but to focus instead on the properties of the exciton energy eigenfunctions and the kinetics of trapping the exciton for the simple structural situations that I considered then and that Hemenger and I (Hemenger and Pearlstein 1973) considered a little later. All were basically one-dimensional (except possibly for the placement of the trap), simple linear chains or rings of interacting molecular transition dipoles. We chose these structures for ease of theoretical treatment, not because we were prescient with respect to antenna structural models of the decade just past – see the next section.

I considered first a linear chain of N dipoles with identical nearest-neighbor interactions. The exciton states on this structure are standing waves, not unlike the sound-producing vibrational waves of a stringed musical instrument, except that the exciton waves are probability amplitudes. If the dipole interactions are negative, the exciton state of lowest energy corresponds to the fundamental string frequency, i.e. exactly one-half wavelength fits on the chain (string) with the maximum amplitude (antinode) occurring at the center. For the chain of dipoles, numbered from 1 to N left to right (Figure 2), the exciton wave amplitude is described by the sine curve, $\sqrt{\frac{2}{N+1}}\sin\left(\frac{\pi m}{N+1}\right)$, where m is the dipole number. The square root factor to the left of the sine function ensures that the sum of the squared wave amplitudes from m = 1 to N is unity, the required result if the excitation is somewhere within the chain of N dipoles.

If N is large, then at the left end of the chain, where m = 1, the sine becomes approximately equal to its argument, i.e. the exciton wave amplitude there approximately equals $\sqrt{\frac{2}{N+1}}\left(\frac{\pi}{N+1}\right)$. The excitation probability at m = 1 is the amplitude squared, hence $2\pi^2/(N+1)^3$. Because $\sin\left(\frac{\pi}{N+1}\right) = \sin\left(\frac{\pi N}{N+1}\right)$, the result is the same at the right end (m = N). In my coupled treatment (Pearlstein 1968, 1972), as long as transfer into the trap itself is the kinetic bottleneck, for a trap placed to the left of m = 1 or to the right of m = N (assuming only nearest-neighbor interactions), the migration-and-trapping rate is proportional to this squared amplitude. The reciprocal of the rate, the lifetime, is then proportional to $(N+1)^3$. In other words, the trapping process takes even longer than under diffusion-limited hopping transfer, for which the lifetime is merely proportional to N^2, and very much longer than under trap-limited hopping transfer, for which the lifetime is just proportional to N.

When I first saw this result, I was astonished. It was just the opposite of what Avery et al. (1961) had been anticipating and generally counterintuitive from the viewpoint of 'fast' exciton transfer adherents. Of course, I had selected a structure – a linear chain of dipoles with a trap at one end (Figure 2) – in which the trap was located close to a node of the exciton standing wave, a point of complete destructive interference between the left- and right-directed traveling waves that constitute the standing wave. What would happen in my coupled treatment if the trap were adjacent (but lying off the chain itself) to the antinode (Figure 2)? I considered the latter case (Pearlstein 1972) and found that, as long as the transfer-to-trap step remained the kinetic bottleneck, the excitation probability for dipole number (N + 1)/2 (assuming N to be an odd number) is $2/(N+1)$, yielding an overall trapping rate $(N+1)^2/\pi^2$ times larger for the center-trap than for the end-trap on the same chain of dipoles.

That certainly seemed a respectable degree of trapping-rate enhancement due to phase coherence, until I realized that for any given transfer-to-trap rate constant (still small enough to be a bottleneck) it was a mere factor of two greater than in the case of trap-limited hopping transfer. What if the N dipoles were laid out in the form of a closed ring (Figure 2) rather than an open chain, so that the excitons are traveling waves rather than standing waves? In that case (Hemenger and Pearlstein 1973), the exciton wave

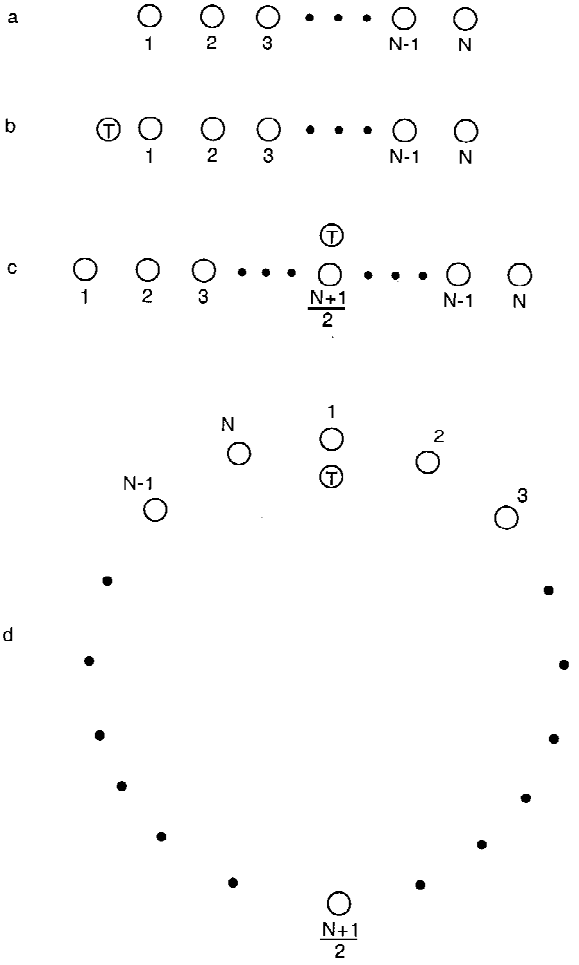

Figure 2. Schematic diagrams of linear arrays of resonantly interacting transition dipoles. Open circles designate positions of individual numbered dipoles. An open circle containing a 'T' marks the position of an exciton-trapping site. A series of black dots signifies an unspecified number of dipoles. (a) Open chain without a trap. (b) Open chain with a trap at one end. (c) Open chain with a central, off-array, trap. (d) Closed ring with an off-array trap. In (c) and (d) the number, N, of interacting transition dipoles is assumed to be odd. In (d) the placement of the trap adjacent to the dipole marked '1' is arbitrary – see text.

amplitudes are the complex exponentials, $\frac{e^{2i\pi km/N}}{\sqrt{N}}$, where the integer k (= 1, ... , N) labels the exciton energy level. Thus, regardless of energy level, the (absolute) squared amplitude is simply 1/N, meaning that in any level, for a bottlenecking trap adjacent to any dipole, the trapping rate is *exactly* the same as for trap-limited hopping transfer.

For these simple model systems and attendant assumptions, the answer to Clayton's question is that a factor of two enhancement in the overall trapping rate might be achieved with Frenkel excitons as compared to randomized-phase excitation, if the trap is near the antinode of a standing exciton half-wave on an open chain of transition dipoles. Somehow I doubt that this would have satisfied Avery, Bay, and Szent-Györgyi.

Current relevance

Bay and Pearlstein (1963c) is certainly of historical interest now, especially since it spawned a rich literature, in part as reviewed here. See also Lakatos-Lindenberg et al. (1972), Hemenger et al. (1972) and Pearlstein (1982, 1996). The N log N dependence specifically may have some relevance to photosynthesis research now for extended-membrane-antenna systems, if N, the number of core antenna chlorophylls per active reaction center, is large enough that the migratory contribution to the migration-and-trapping lifetime begins to dominate.

Given the established structure of chlorophyll ring antennas (McDermott et al. 1995), the simple structures my collaborators and I studied theoretically in the late 1960s and early 1970s – see also Hemenger et al. (1974) – in connection with the trapping of Frenkel excitons certainly have some current relevance. I say this not so much because I think actual Frenkel exciton states contribute significantly to trapping (although I believe this is still not an altogether closed issue), but because there is compelling evidence that such states are the ones initially created, at least by monochromatic excitation of the Q_Y transition (van Oijen et al. 1999). Insofar as the ring antennae function independently and have circular symmetry, the exciton eigenfunctions are certainly traveling waves. If, however, the symmetry is broken in certain ways (McGlynn et al. 1996) – consistent, of course, with the X-ray structural models – standing-wave eigenfunctions are possible. I treat the latter contingency in some detail in a forthcoming paper (Pearlstein, in preparation).

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