From Förster resonance energy transfer to coherent resonance energy transfer and back

A wheen o' mickles mak's a muckle

"Like van Niels' concept of photochemical oxidoreduction, the idea of the photosynthetic unit has become a cornerstone of current descriptions of photosynthesis." (Roderick K. Clayton, 1965)

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ABSTRACT

Photosynthesis converts solar energy into chemical energy. It provides food and oxygen; and, in the future, it could directly provide bioenergy or renewable energy sources, such as bio-alcohol or hydrogen. To exploit such a highly efficient capture of energy requires an understanding of the fundamental physics. The process is initiated by photon absorption, followed by highly efficient and extremely rapid transfer and trapping of the excitation energy. We first review early fluorescence experiments on *in vivo* energy transfer, which were undertaken to understand the mechanism of such efficient energy capture. A historical synopsis is given of experiments and interpretations by others that dealt with the question of how energy is transferred from the original location of photon absorption in the photosynthetic antenna system into the reaction centers, where it is converted into useful chemical energy. We conclude by examining the physical basis of some current models concerning the roles of coherent excitons and incoherent hopping in the exceptionally efficient transfer of energy into the reaction center.

Keyword list: FRET (Förster Resonance Energy Transfer), CRET (Coherent Resonance Energy Transfer), energy migration, photosynthesis, reaction center, excitons, trap limited. transfer-to-trap limited, coherent transfer, incoherent transfer, dephasing

1. INTRODUCTION

The mechanisms of energy transfer (perhaps better described as energy migration) from the location of photon absorption in an antenna system of a photosynthetic system to the reaction center, and the subsequent kinetics of electron transfer, involve kinetic processes on a very large time scale. The absorption of a photon takes place, as usual, in a sub-femtosecond time scale. Once the energy of the photon, $h\nu$, has been absorbed by either an individual chromophore, or by a group of strongly interacting chromophores, the energy migrates rapidly from this initial location of excitation to the reaction center. The mechanism of this energy migration, and the dependence of this energy migration on the structure

and dynamics of the photosynthetic system, has been a major topic of research for a long time. At present, the modern physical models describing this energy migration, and the subsequent capture (trapping) and electron transfer in the reaction center, are highly computational and the complexity of the theories mirror the complexity of the highly organized and multi-functional biological system. For the same reason, experiments are difficult to unambiguously interpret in terms of the whole process of photosynthesis under natural biological conditions of an intact photosynthetic system, especially considering the broad temporal span of dynamic events. The focus of this paper is to follow the historical development of ideas about how the energy migration takes place, and to describe a few of the fundamental physical processes on which the modern theoretical accounts are based. This is not a review of the present state of affairs, or a detailed comparison of the different points of view of different research groups.

2. THE CONCEPT OF THE PHOTOSYNTHETIC UNIT: ANTENNA AND REACTION CENTERS

In 1932, Robert Emerson and William Arnold [1-2] did a pioneering experiment where they measured the maximum oxygen evolution from suspensions of a model organism of the time, a green alga *Chlorella pyrenoidosa*, in brief saturating and repetitive light flashes, separated by an optimum dark period. Contrary to the expectation of that time, they observed that about 2,400 chlorophyll (Chl) molecules were required to produce one oxygen molecule. They wrote [2]: "*We need only suppose that for every 2480 molecules of chlorophyll there is present in the cell one unit capable of reducing one molecule of carbon dioxide each time it is suitably activated by light.*" At that time, it was assumed, based on the ideas of Otto Warburg and Richard Wilstätter that photosynthesis began with oxygen coming from an activated molecule of carbon dioxide. In 1934, Arnold and Henry Kohn [3] examined all the possible errors in the earlier experiments and confirmed the existence of a "unit" of ~2400 Chl/oxygen, calling it a "**chlorophyll unit**", which was present in several photosynthetic systems they had examined. In 1936, Kohn [4] concluded that the **absorbing unit** was a fraction of that number, closer to 500 Chls, consistent with the idea of that time that 4 photons were needed for oxygen evolution. In the same year, Hans Gaffron and Kurt Wohl [5-6] understood the full importance of these measurements. Gaffron and Wohl [5-6] calculated that in a *Chlorella* suspension, used by Emerson and Arnold [1-2], where oxygen evolution begins immediately upon exposing the samples with weak light, it would have taken an average of an hour or more to collect the number of photons (4-12) on the same chlorophyll molecule necessary for evolving one oxygen molecule; see a 1940 review by Wohl [7]. This paradoxical result could be explained only if we were to have a means of 'funneling' quanta absorbed by different molecules on to one common center where chemistry would begin. Gaffron and Wohl [5-6] asked the question how the quanta absorbed anywhere in the 'unit' (in today's language: the **photosynthetic unit**) is utilized efficiently at the 'center' (in today's language: the reaction center) without loss. Gaffron and Wohl [5-6] imagined that the pigment molecules are packed densely and that an absorbed light quantum on any pigment is exchanged from neighbor to neighbor until it reaches the 'center. *In this picture, 'quanta' themselves were assumed to move around until they find the 'center' where photochemical reaction takes place.*[1] This then was the first concept ever of quantum energy being transferred from one molecule to another, as far as we know. It was, we believe, the origin of the concept of "**Antenna and the Reaction Center**" although these terms were to be only later used (see, e.g., Clayton [8]). Clayton wrote [8] "*The pigment aggregate acts as an antenna, harvesting the energy of light quanta and delivering this energy to the reaction center.*"

The first question that comes to mind is: Is 2400 Chl per oxygen evolution a magic number? Arnold and Kohn [3] obtained even higher numbers (3,200 - 5,000) in a plant *Lemna* sp., in a moss *Selaginella* sp. and in an alga *Stichococcus bacillaris*. On the other hand, Georg Schmid and Gaffron [9], using several plants (e.g., *Nicotiana tabacum*, tobacco) and several algae (*Scenedesmus* D_3*; Ankistrodesmus braunii*) and a cyanobacterium (*Anacystis nidulans*) grown under

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[1] Gaffron and Wohl [6] wrote, as translated by one of us (RMC) from the original German: "During assimilation, more than 1000 chromophores and 1 carbonic acid molecule work together. We see two possible explanations for this. Firstly, it can be imagined that the carbon dioxide and the corresponding photochemical product diffuse, hopping from chlorophyll molecule to chlorophyll molecule, in order to gather the necessary quanta. *Secondly, it is possible that the carbonic acid is bound at a stationary location and becomes reduced at this location, whereby the quanta of energy, which are absorbed at random locations within the assimilation complex, rapidly fluctuate throughout the complex until the necessary number of quanta are eventually trapped at the position where the carbonic acid is located. Upon closer inspection, the first option encounters great difficulties. Therefore, we believe that only the second option is possible.*"[We know that the ideas of the functioning of the carbonic acid as well as the idea that a minimum of 4 photons, instead of 8-12 photons, per oxygen molecule evolved, are both wrong.]

different physiological conditions discovered that the size of photosynthetic units can be of multiple sizes: ~300, ~600, ~1200, ~1800, ~2400, and ~5000 Chl/CO$_2$ fixed (equivalent to O$_2$ evolved). This gives a clue about their physical basis.

3.   WHAT DOES THE PHOTOSYNTHETIC UNIT (PSU) MEAN TODAY?

It is now well established that photosynthetic organisms, whether they be oxygenic or anoxygenic, contain their pigments within multi-protein complexes. Oxygenic photosynthesizers have two pigment systems (Photosystem I (PSI) and Photosystem II (PSII)) and use two light reactions, working 4 times, to transfer electrons from 2 molecules of water to the pyridine nucleotide, NADP$^+$, evolving one molecule of oxygen and producing 2 NADPH; during the same process, ATP is made, using the energy from the proton motive force created across the thylakoid membranes [10-13]. Thus, on the average, one may suggest that each PSII and PSI (both antenna plus reaction centers) would have about 300 Chl molecules. The Emerson & Arnold PSU, thus, has a different meaning now; it then is an integrated, perhaps, a statistical concept, whereas we now have a detailed biochemical and biophysical information on what the PSU is actually made of. In anoxygenic photosynthetic bacteria, there is no oxygen evolution; there is only one light reaction, and the structures of almost all the antenna and reaction center complexes are available. Thus, these structures have now been integrated to produce models of the complete PSU. This has opened the doors to a detailed understanding of the energy transfer events occurring within the PSU (see e.g., Cogdell et al. [14], and Van Amerongen et al. [15], and Şener and Schulten [16]).

Fig. 1 shows the contrast between the pigment networks in the evolutionarily more primitive purple bacterial light-harvesting proteins [17-18] and plant and cyanobacterial photosystem I [19-20].

Fig. 1. Comparison of the pigment arrangements in light-harvesting proteins from anoxygenic purple bacteria and from oxygenic plants and cyanobacteria. Shown in (**a**) is the light-harvesting complex LH-I surrounding a reaction center and in (**b**) the peripheral light-harvesting complex LH-II (bacteriochlorophylls and carotenoids are shown). The regularity of the repeated alpha-beta peptide subunits that constitute the LH-I and LH-II complexes display a stark contrast to the chlorophyll arrangement of Photosystem I shown in (**c**) (solid black: cyanobacterial; semi-transparent: plant with surrounding light harvesting Lhca subunits).
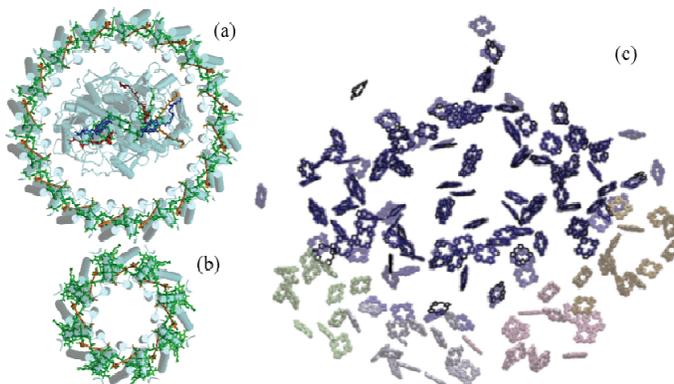
Due to their symmetry, purple bacterial light-harvesting complexes are characterized by a handful of parameters describing pigment site energies and excitonic couplings, whereas PSI displays significant inhomogeneity in its spectral and excitonic behavior [21]. Notably, at low temperatures the quantum efficiency of PSI becomes strongly wavelength dependent as an excitation can get 'trapped' in pools of Chls without resonant coupling to the RC (reaction center). At room temperature, thermal disorder results in a broadening of line shapes of pigments and a subsequent spectral overlap resulting in high quantum efficiency.

It appears that evolution of light-harvesting complexes favored a greater packing density of pigments: the Chl per amino acid ratio in cyanobacterial PSI is 1:27. For a corresponding system for purple bacteria consisting of a RC-LH1 complex and two accompanying LH-II complexes this ratio is only 1:40 [16]. Both systems display high quantum efficiency since Förster radius is much larger than the typical inter-(bacterio)chlorophyll separation. For a general review on PS II of cyanobacteria and plants, see Govindjee et al. [12].

4.   EARLY IDEAS OF ENERGY TRANSPORT

The transport of energy from one location and form to another is a common theme in all areas of physics from astronomy to nuclear physics. For instance, gases can exchange energy between individual molecules by collision, and in some cases by non-radiative transfer. In fact, the original observation of energy transfer over distances larger than the sum of the radii (non-collisional) of the interacting molecules (atoms) was one of the first indications of dipole-dipole resonance transfer; see Clegg [22] for a review of these early experiments and references. Subsequent to these studies, it became apparent through fluorescence polarization experiments [23-25] that energy could be transferred from an excited

molecule to nearby neighboring molecules in solution over distances far exceeding the molecular diameters. The original account of this transfer [24-26] was also in terms of dipole-dipole interactions. The explanation of transfer of energy between two molecules in solution by the J. & F. Perrin correctly involved dipole-dipole intermolecular interaction, but their analysis considered two identical interacting molecules with two states isolated from the effects of the environment that had infinitely narrow energy breadths (these are conditions very similar to the formation of excitons (see section 8), but the Perrins' analysis was somewhat different). As a result their prediction of the distance dependence for energy transfer was much too large. As we will discuss below this was because they did not consider that the conditions of these experiments involved much broader energy levels where the excited state configuration was at equilibrium with the environment (e.g. solvent); that is, the excited molecules undergo multiple collisions with the environment before energy transfer takes place, and this leads to phase decoherence resulting in incoherent transfer. Theodor Förster realized this error, and derived the correct rate of incoherent energy transfer that is operational for molecules in condensed matter interacting with Coulomb interactions, which he approximated at larger distances as point dipole-dipole interactions [27-28]. This realization allowed him to apply a probabilistic treatment of the energy level overlap between the excited (donor) and ground (acceptor) states of the molecules (in more sophisticated terminology, the conditions of such energy transfer are those favorable for applying Dirac's Fermi Golden Rule – see section 7 below). Förster knew of the work of the Perrins and the experimental measurements of polarization of dyes at higher concentrations [24-25]. In his original publications he also mentioned the need to invoke energy migration to explain the efficiency of photosynthesis.

It is not generally appreciated that the correct mechanism and theory (identical to that of Förster) were derived earlier by Arnold and J.R. Oppenheimer (see [29]). Interestingly, the work of Arnold and Oppenheimer was inspired by the high efficiency of photosynthesis. Emerson was carrying out research on the quantum efficiency and the action spectra of photosynthesis in cyanobacteria (then called blue-green algae) and green algae , but published in 1942 and 1943 [30-31]. Arnold, who had taken a quantum mechanics course with Oppenheimer earlier, discussed this phenomenon with him, who immediately made an analogy with nuclear internal conversion [22, 29, 32]. Oppenheimer published the basics in a short abstract of a talk presented by him at a Physical Society meeting dealing with nuclear physics [29]; for some reason he did not mention Arnold in the abstract. The cursory abstract presented no details, and very probably no one in the audience was actively engaged in photosynthesis. Knox [33] has presented a detailed account of Arnold and Oppenheimer's contributions. Knox writes: "*Oppenheimer argued that resonant transfer would take place, driven by the strong near zone field of the initially excited molecule's transition moment. As an irreversible process, such a mechanism would have a rate proportional to $\boldsymbol{R}^{-6}$, where R is the intermolecular separation*". In the 1941 abstract of Oppenheimer (which was based on the earlier experimental observations by Emerson (cf. [34]) we find a clear statement that acknowledges that a chlorophyll a molecule would receive energy absorbed by the blue pigment phycocyanin molecules in cyanobacteria. It was only 9 years later that Arnold and Oppenheimer [32] published their long-delayed paper; they predicted a hopping time of excitation energy of about 2 ps when the distance between the donor and the acceptor molecule was ~ 15 Å. By then the classic FRET (Förster Resonance Energy Transfer) theory [27-28] had been published, and indeed cited by Arnold and Oppenheimer [32]. Based on our own reading of the literature and the paper by Knox [33], we believe that Arnold was the first one to apply the concept of resonance energy transfer in photosynthesis (see [34]). However, Forster's original derivations and analyses [27-28] (which also mentioned Emerson's work on photosynthesis) had the greatest impact on the theory of excitation energy transfer in photosynthesis.

In the mechanism of Arnold and Oppenheimer, and also of Förster, the terminology of "incoherence" refers to the complete vibrational relaxation of the excited chromophore (called the donor) before the energy is transferred. The vibrational relaxation of the excited molecule is due to the interaction with its environment. At room temperatures it is easy to show that this relaxation takes place in only a few picoseconds (this is approximately the time for heat diffusion over molecular distances), before the intermolecular energy transfer takes place. For the conditions assumed in these early theories, the vibrational relaxation of the excited chromophore (and collisional interactions with the environment – e.g. solvent) completely relaxes any coherent process that could take place with the excited molecule if it were excited in a vacuum, or at very low temperatures. Since Förster's original publications, this mode of energy transfer has become known as Förster Resonance Energy Transfer (FRET); in the following we will use FRET to refer only to this mode of energy transfer. Förster gave us a theoretical description to interpret experiments of energy transfer between coupled molecules in terms of experimentally determined spectroscopic properties of the non-interacting donor and acceptor molecules (the overlap integral), and this has led to an immensely extensive literature. FRET has been applied successfully in all areas of experimental science, especially in biology.

5. SENSITIZED FLUORESCENCE: EVIDENCE FOR ENERGY TRANSFER IN PHOTOSYNTHESIS *IN VIVO*

5.1. 1940s and 1950s

The first recorded case of 'sensitized fluorescence', and energy transfer is that of G. Cario and James Franck in 1922 [35] when they discovered that in a mixture of mercury and thallium vapor, thallium (to be called the acceptor) emitted fluorescence when mercury (to be called the donor) was excited at 253.6 nm. It was not until 1943 that the first clear example of sensitized fluorescence was reported in photosynthesis; in the diatom *Nitzschia closterium,* Dutton et al. [36] demonstrated almost 100 % excitation energy transfer from fucoxanthin (fucoxanthol) to Chlorophyll (Chl) *a*, because when fucoxanthin was excited, it led to the same amount of Chl *a* fluorescence as when only Chl a was excited. This was also the first clear example of the light-harvesting function of one of the carotenoids *in vivo* (see Dutton [37] and Govindjee [38]). Three years later, but independently, Wassink and Kersten (1946 [39]) obtained the same conclusion with another diatom *Nitzschia dissipata*. These experiments were the first to prove that excitation energy transfer takes place from one pigment to another in photosynthetic systems.

Louis N. M. Duysens ([40-41]) provided the most systematic studies on excitation energy transfer in (i) purple bacteria *Chromatium* and *Rhodospirillum molischianum* (almost 100% transfer from bacteriochloophyll B800 to B850 to B890; about 50 % from carotenoids to B890); (ii) green alga *Chlorella* (100% transfer from chlorophyll b to chlorophyll a); (iii) red alga *Porphyridium cruentum* (about 80 % from phycoerythrin to phcocyanin, and about 80% from phycocyanin to chlorophyll a); and (iv) blue-green alga (a cyanobacterium) *Oscillatoria* (about 80% from phycocyanin to chlorophyll a). In addition, Duysens [40-41] discovered the existence of two types of chlorophyll a, one fluorescent, and another non-fluorescent. C. Stacy French and V.M.K. Young [42] had independently discovered excitation energy transfer in red algae from phycoerythrin to phycocyanin and from phycocyanin to chlorophyll a.

William Arnold and E. S. Meek (1956 [43]) provided the first clear evidence for excitation energy migration among chlorophyll a molecules through their observations of depolarization of chlorophyll a fluorescence. The degree of polarization of the fluorescent light in Chlorella cells was so low (0.030) that the inevitable conclusion was that fluorescence must be emitted by chlorophyll molecules that did not themselves absorb the exciting light, that is, there must be efficient energy migration (transfer) among chlorophyll a molecules in photosynthetic units. The very first observation of the time of excitation energy transfer was made in 1958 in the laboratory of Eugene Rabinowitch when Steve Brody [44-45] (see [46] for a minireview) measured the delay time in seeing chlorophyll a fluorescence when phycoerythrin was excited in the red alga *Porphyridium cruentum* with a ns flash of green light; the time, of energy transfer from phycoerythrin to chlorophyll, via phycocyanin, was in the range of ~500 ps, as measured with the very first direct flash lifetime of fluorescence instrument that Brody had built. For an improvement and extension of this work, see Tomita and Rabinowitch [47]. It was in 1978 that Sir George Porter and co-workers [48] confirmed and extended these observations, using a streak camera.

5.2. 1960s—1990s

During this period, extensive research was done on excitation energy transfer and on the action (excitation) and emission spectra of chlorophyll a fluorescence, not only at room temperature, but down to liquid helium temperature (4K). See reviews [49-52]. Experiments in the laboratory of one of us (G) revealed that when Photosystem II (PS II) is closed, at room temperature, either by high light intensity or by the use of an inhibitor Diuron (that blocks electron transport beyond this system), a new emission band appears at around 693 nm [53-54], and the polarization of chlorophyll a fluorescence decreases [55-57]. This suggested increased excitation energy migration in the antenna. Already in the 1960s, soon after Brody [58] had discovered a new emission band at ~720 nm at 77K in the green alga Chlorella, it became clear that at 77 K, there are at least 4 emission bands: F 685 (from PS II); F695 (from PS II); F720 (from PS I) and F735 nm (from PS I) (see e.g. [59-64]). More importantly, remarkable changes in emission spectra and in excitation energy transfer were observed, in green algae, red algae, and cyanobacteria down to 77 K (and even 4 K) [59, 61-65]. Attempts were made to relate these observations to the possible Förster Resonance Energy Transfer (FRET), but the complexity of the intact system and the lack of detailed information on the parameters did not allow any firm conclusions. Another question, relevant to excitation energy migration or transfer that one of us (G) had asked, is whether there was a so-called "lake model" (a term coined by G. Wilse Robinson; here excitation energy moves freely among many units) or "separate package model " (that is, where there is no energy exchange between individual units). This is a question that Joliot and

Joliot had dealt with in 1964 (see [66]) and had concluded that the probability of energy transfer from inactive units to active units was ~0.55. Measurements of chlorophyll a fluorescence lifetime as a function of fluorescence intensity during the Kautsky transient (fluorescence transient during continuous illumination) confirmed the concept that in intact cells and in thylakoids, excitation energy is shared extensively among several PSII units (see e.g. [67-68]).

A rather current picture of this area of research is included in several chapters in two books [69-70] and in a recent special issue of Photosynthesis Research. [2]

5.3 Excitation energy cascade, examples

When ultrafast (femtosecond to picosecond) light flashes are used to excite donor molecules, we can measure directly the time of excitation energy transfer from the donor to the acceptor molecule: as the donor fluorescence decreases, the acceptor fluorescence increases. This can be observed when the donor and acceptor molecules have different absorption and emission spectra. In a red alga *Porphyridium cruentum*, a beautiful cascade of excitation energy transfer, within 100 ps range, is observed from phycoerythrin (F575, fluorescence emission at 575 nm) to phycocyanin (F645) and on to allophycocyanin (F 665); and by 500 ps, the excitation is fully on chlorophyll *a* (F685). Similar, although quantitatively different, results were obtained for excitation energy transfer from phycocyanin to allophycocyanin to chlorophyll a in cyanobacteria *Anacystis nidulans* and *Anabaena variablis* [71-75]. This energy transfer pathway must follow the FRET mechanism. Recently, Komura and Itoh [76] have summarized their results on excitation energy transfer from one spectral form of chlorophyll *a* to another in spinach, a higher plant, at 77 K and 4K. These measurements, made using a streak camera in single-photon counting mode, showed that chlorophyll a species fluorescing at 677 nm (F677) transferred excitation energy to F 685 within 5 ps; from F685 to F695 in ~180 ps; and from F680 to F689 in ~30 ps at 77K; cooling the samples to 4K led to a slowing down of these transfer times by ~ 5 fold! Using a streak camera, Gilmore et al. [77] have presented global spectral-kinetic results on barley, another higher plant, at room temperature, but only when PSII reaction center is being closed (all the intermediates beyond PSII become reduced) by high light: lifetimes of Chl a fluorescence increase from 250-500 ps to 1250-2500 ps, accompanied by changes in excitation energy transfer (or redistribution) among the two photosystems.

6. MECHANISMS OF ENERGY TRANSPORT IN PHOTOSYNTHESIS

Originally it was hypothesized that energy migration in photosynthesis took place only by normal FRET; that is, under conditions of fully incoherent transfer at distances that are long enough to allow for the point dipole approximation to be effective. Förster's mechanism is applicable to situations where the coupling between the donor and acceptor is through a transition dipole–transition dipole interaction, and the molecules are capable of optical transitions between the respective energy levels. The excitation energy is assumed to be completely on either the donor or acceptor. The excitation energy in a photosynthetic system was hypothesized to migrate by diffusion in a stochastic manner by a hopping mechanism. The energy would either eventually be captured by the reaction center, or depart from the sample in a nonradiative (heat) or radiative (fluorescence) pathway. According to the hopping model, each transfer step is independent of the previous one, similar to a random walk. Experimentally one observes the fluorescence decay of the sample or the double pulse absorption spectra from which one can deduce quantitatively the different participating rate parameters. The rates of FRET, fluorescence and heat (nonradiative) decay all act in direct first order competition with each other at every transfer step, leading to the observed rate of fluorescence emission if the interacting molecules are different, or to the rate of anisotropy decay if the molecules are identical. Early extensions of this dipole-dipole Förster mechanism were developed once it became known that many molecules making up the photosynthetic structures are highly organized and very close together, so that the approximation of a point dipole interaction may no longer be valid. One way to extend the Förster theory is to retain the basic premise of Förster transfer, but to model the intermolecular interactions with extended charge distributions beyond the point dipole approximation. An additional suggestion made

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[2] Messinger, J., Alia, A. and Govindjee (eds), "Special Issue: Basics and Applications of Biophysical Techniques in Photosynthesis and Related Processes," Part A and Part B," Photosynth. Res. **101** (Nos. 2 and 3), see reviews on Fluorescence by Streak Camera, by M. Komura and S. Itoh (pp. 119-113); on Fluorescence Lifetimes by U. Noomnarm and R.Clegg (pp. 181-194); on Photon Echo Studies by E.L. Read, H. Lee and G.R. Fleming (pp. 233-243); and on Spectral Hole Burning by R. Purchase and S. Volker (pp. 245-266   ) and Photosynth. Res. **102**(Nos. 2 and 3), see reviews on Fluorescence Imaging by Y.-C.Chen and R.M. Clegg (pp. 143-155), by Z. Petrasek et al. (pp. 157-168   ), and by Z. Benediktyova and L. Nedbal (pp. 169-175); and on Theory of Excitation Energy Transfer by T. Renger (pp. 47-485) (2009).

by D. Dexter and coworkers [78-79], involves electron exchange mechanisms when there is an overlap of atomic orbitals, and the transfer of energy is also possible between two molecules with forbidden optical transitions. Dexter also considered higher order expansions of the Coulombic interactions. However, it became apparent - due to the very close association of many participating chromophores in a photosynthetic system - that additional mechanisms of transfer should be considered.

Further extensions of the original Förster transfer were proposed in order to take account of the variations of the coupling between molecules in photosynthetic systems from strong to very weak; the latter being the original FRET mechanism of Förster. New modes of energy transfer between molecular systems were introduced to take into consideration that the intermolecular coupling could be stronger than assumed for FRET, and this brought into consideration exciton theory (see e.g. [80]). This transfer mechanism might be called Coherent Resonance Energy Transfer, or CRET, to distinguish it from FRET. The question then arose: how does one describe the broad variation of intermolecular interaction energies that are found in photosynthetic structures? Before proceeding to further developments, it is worthwhile to dwell on an early presentation by Förster [80] and to delve a bit into the basic quantum mechanical ideas behind excitons.

7. A FEW COMMENTS ABOUT THE FRET MECHANISM (VERY WEAK COUPLING)

Förster pointed out from the beginning that his FRET theory did not contain any quantum parameters, and he also showed that one can derive his famous equations describing FRET classically. The Perrins had also initially developed their theory of energy transfer based on a classical model of interacting dipoles. On the other hand, of course, it is theoretically more correct to derive the theory quantum mechanically, as Förster did in his second paper of 1948 using time-dependent perturbation theory [28]. Arnold and Oppenheimer also used time-dependent quantum mechanics (QM) perturbation theory to derive their expression for FRET in 1941 [29] (although the derivation was not reported in the abstract and Arnold was for some reason not an author, as mentioned above) and gave a thorough QM derivation in their 1950 publication [32]. Even the earlier theoretical investigations of energy transfer in plasmas and gases [22] made use of the newly developed theory of quantum mechanics to derive their expressions of energy transfer. All of these theoretical treatments used the ideas of the Fermi Golden rule (which had not yet been christened under this name, but had been given and explained already by Dirac in 1927 [81]). In the context of the present discussion, the Fermi Golden rule (which should more appropriately be called Dirac's Fermi Golden Rule) pertains, provided that there is complete relaxation of the excited donor molecule, to a state of quasi vibrational equilibrium before the energy transfer to the acceptor molecule takes place. This means that the intermolecular coupling interaction is "very weak" compared to the vibrational energy level widths, to the extent that the spectroscopic characteristics of both molecules are identical to that of the separate molecules in the absence of the other. The notation specifying the strength of the intermolecular coupling varies in the literature – here we refer to the notation often used to refer to Förster transfer – in effect the notation "very weak" refers to the limit of weak coupling, so that the participating molecules retain their spectroscopic individuality. Although Förster realized and mentioned the vagueness of this notation, he used it often, and it is also used in much of the present literature to refer to Förster transfer (FRET).

8. EXCITONS – A BASIC VIEW

The field of excitons is well developed and extends over a large range of disciplines. It is a quantum mechanical concept. The description of excitons, their formation, structure, dissipation and decoherence kinetics requires advanced theoretical descriptions for complex systems such as photosynthetic structures. However, the basic idea is straight forward and is simply demonstrated by considering only two molecules. The idea is that when a sample containing closely associating chromophores, which are coupled with certain strengths of interaction, is excited, the excited state cannot be described by the excitation of a single chromophore alone, but the excitation is simultaneously extended over more than one molecule (delocalized). The state of the system is a combination of wave functions of both molecules. The excited state is described by a linear sum over product wave functions; the product wave functions are products of the individual, independent molecular wave functions. One member of each product wave function of the sum is for the excited state of one of the individual molecular wave functions; the other individual wave functions of each product are ground state wave functions. The summation extends over all product functions with excited states of all separate molecules contributing to the molecular aggregation forming the excitons (we do not here worry about electron spins or parity of the total wave function). The coefficients of each product component of the summation represent the contribution of each component to the exciton's structure (the coefficients are time dependent, in general). Actually it is

the square of each component that is proportional to the relative population of the respective component (at any time). A beautiful description of such wave functions for such an assembly of particles (molecules) has been given by Dirac in his usual crisp and exceptionally clear style [82] : "*The general ket* [wave function] *for the assembly is of the form of a sum or integral of kets* [...]*, and corresponds to a state for the assembly for which one cannot say that each particle is in its own state, but only that each particle is partly in several states, in a way which is correlated with the other particles being partly in several states*".

The simplest case to consider is two coupled identical molecules (they need not be identical; for simplicity we assume this).Then the excited energy of the total exciton system for two molecules splits into two new levels, one above and one below the energy level of the separate molecules. If more molecules are involved in the exciton structure, the energy splitting is more complex, but the total wave function is still represented by the sum of products of molecular wave functions. Depending on the orientations and distances between the individual molecules of the coupled molecular structure, new oscillator strengths arise (compared to the absorption spectra of the individual of molecules) – this can lead to large variations in the observer amplitude of spectroscopic transitions, and these spectroscopic changes are diagnostic of the existence of exciton structures. This is a purely quantum effect, and there is no parallel classical model. This basic description of coupled systems is by no means limited to excitons – such descriptions of quantum assemblies are ubiquitous throughout many different fields of physics (see for instance a nice simple description of some fundamentals in the famous physics textbook series by Feynman *et al.* [83]).

The first person to demonstrate with wave mechanics the QM solution for two molecules that are coupled by a perturbation was Schrödinger in 1927, in one of the first papers in his series of publications demonstrating his newly developed Schrödinger Equation [84]. The title of this paper is "Energie Austausch nach der Wellenmechanik" – "Energy transfer according to wave mechanics". In this paper Schrödinger used the method of variation of constants to solve the coupled differential equations arising from his theory (the variation of constants was also developed by Dirac [81]) in order to demonstrate how to solve the coupled molecular system. This problem had been treated earlier with matrix mechanics by Heisenberg in 1926, "Mehrkörperprobleme und Resonanz in der Quantemmechanik" – "Multi-body Problems and Resonance in Quantum Mechanics" [85]. Both Heisenberg and Schrödinger described in these two papers how to use their respective quantum formulations to treat coupled quantum systems; also, they both emphasized that the behavior of such coupled systems (the energy level splitting and the oscillatory transfer of energy) was solely quantum effects. It is clear from Schrödinger's title that the coupling leads to a transfer of energy between the participating separate quantum systems, and Heisenberg's title indicates the resonance phenomenon.

When one considers the simplest example of just two interacting quantum systems (just *two states* for each system – ground and excited states - and *no interaction* with surroundings), both quantum formulations of Schrödinger and Heisenberg lead to an oscillation; the energy is transferred periodically from one system to the other in a time-dependent sinusoidal fashion. These oscillations were much later christened Rabi oscillations, after I. Rabi who investigated similar effects in the NMR time range [86]. The oscillation is a result of the phase coherence of the two quantum systems, and the frequency depends on both the energy level differences of the two molecules and the size of the intermolecular interaction. If there is some sort of damping that influences the two systems (for instance, interaction with a fluctuating molecular surrounding – e.g. solvent or protein environment), the two systems will lose coherence; then the system will no longer oscillate periodically, and the oscillation amplitude will die out, and the phase coherence will become lost. The fluctuating collisions of the environment are said to "dephase" (randomize) the two coupled systems; this also leads to a time-dependent localization of the delocalized excitons. If the decoherence takes place rapidly compared to the coherent oscillations, the two systems are still coupled, but the transfer of energy between the two systems now takes place through a completely incoherent mechanism (this is the case for Förster transfer). The actual kinetic effect of the dephasing interactions of the environment depends on the magnitude of the environmental interaction as well as on the time between collisions (or vibrations of the surrounding environment). Of course, for muli-atom molecules the vibrations of the molecules themselves can also lead to decoherence. Obviously the rate of decoherence will depend on the temperature; very low temperatures will retain the coherence longer because the interference of the collisions from the surrounding fluctuating environment is slower and lower in amplitude at lower temperatures. Because the frequency of collisions is $>10^{12}$ s^{-1} at room temperature, the coherence time is very short under normal temperatures conditions of photosynthesis. The Gaussian decoherence rate is proportional to the square root of the temperature, $\tau_g^{-1} \propto \sqrt{T}$, assuming incoherent motions of the bath. Using a similar relationship for estimating the dephasing rate for a reasonable reorganization energy (of 80 cm^{-1}) for chlorophyll in a photosynthetic system, it has been

estimated that $\tau_g = 60$ fs at 77 K, and therefore 30 fs at 298 K [87-88]. If correlated protein environments and phonon-induced coherent transfers are present, perhaps this time can be extended [87]. The question is: Is this dephasing time sufficient so that coherent energy transfer processes contribute significantly to the overall efficiency of photosynthesis?

The simple model of two interacting molecules, together with one quantum of excitation, demonstrates much of the basic physics of excitons. For photosynthesis, the important point is that depending on the strength of the coupling and the timing and strength of the surrounding collisions, the excitation energy can be delocalized over more than just one molecule. For strong coupling and many interacting molecules, the delocalization can extend over several molecules. Since the oscillatory behavior arising from coherence is extremely fast (in the femtosecond region) the energy is distributed almost immediately (in a wave-like manner) over much larger distances than the diameter of just one molecule, and this can lead to a sizable acceleration of energy transfer (the transfer can take place within sub-picoseconds over the length scale of the excitons). In addition, even if the exciton does not extend over an entire highly organized macromolecular structure, as found in many photosynthetic systems, a partially localized exciton can diffuse within and throughout the coupled macromolecular aggregate. Of course, decoherence will rapidly diminish this distance, so there is a competition between the transfer of energy through the excitonic structure and the decoherence kinetics. Eventually the environmental interactions will lead to complete decoherence and localization of the excitation energy on one molecule, and this eventually leads to Förster transfer, or incoherent transfer.

It is also possible to transfer energy between two excitonic structures; this transfer takes place in a Förster-type incoherent manner, because the two excitonic structures are not in coherence. We will not discuss this; although, this is one of the steps in the transfer of energy from the antennae to the reaction center.

Much of the theoretical work and modern experimentation (see references in sections 11 and 12) in the sub-picosecond range are aimed at sorting out the contributions of the different levels of coherent and incoherent (or mixed) energy transfer to the efficiency of photosynthesis, or more specifically to the efficiency of energy migration. Of course, the photosynthetic molecular systems involve many participating molecules, and the chromophores are tightly coupled to proteins. Only a few structures of partial photosynthetic systems are known to near atomic resolution. Even if the structures are known, it is a major and very difficult challenge to calculate the expected behavior and overall kinetics of transfer from the antenna to the reaction center. In addition, because the systems are so large with so many subsystems, experiments on biologically functional systems are very difficult. Recently, measurements of spectroscopic signals in the femtosecond range have become possible, and fast pulse lasers and modern detection circuitry are available; and exciting data is becoming available over a large time range. It is also becoming apparent that the different photosynthetic systems, such as photosynthetic bacteria or green plants, have very different properties even in these fast time ranges, and probably the different systems utilize the possibility of excitonic transfer to very different extents, or at least in different manners.

9. FÖRSTER'S UNIFYING VIEW OF ENERGY TRANSFER WITH VARYING STRENGTHS OF INTERMOLECULAR COUPLING

The first person to unify the theoretical models of strong to very weak coupling was Förster himself [80]. The title of his manuscript was "Delocalized Excitation and Excitation Transfer". He points out that it is common in many systems that the ground state properties are additive, but the excited state properties behave differently from the simple summation of the individual component properties. This can be seen in their absorption and emission characteristics. Two of his sentences sum up the topic of his paper: "The reason for this [differences in the spectral and photochemical properties from the separate components] is that in excited states the electronic excitation is not completely localized within one or the other of these components. The excitation may be completely *delocalized* and spread out over the whole system or, in a less drastic way, it may be localized only temporarily, but *transferred* from one component of the system to another.". The italics are Förster's. This sums up quite a bit of present research on energy migration in photosynthesis. The rest of his article is concerned with showing how in his opinion the different cases are actually manifestations of the same underlying physical phenomenon. The differences in the theoretical descriptions lie mainly in the strength of the interaction between molecules, and the comparison of the coupling strength to the width of the electronic and/or vibrational energy levels of the molecules. The strength of coupling distinguishes the quantum mechanical characteristics of the energy transfer kinetics.

10. THE SLIDING SCALE OF COUPLING STRENGTHS AND ENERGY TRANSFER KINETICS – VERY WEAK TO STRONG COUPLING

The discussion above of excitons and Förster transfer describes only the very basic physical origins of different modes of energy transfer. But this suffices for the following discussion of the possible roles that different mechanisms of energy transfer play in the transfer of energy from the antenna structures to the reaction centers. This is the same as asking: What are the coupling strengths between chromophores, and how extensive is dephasing before the transfer takes place?

It has been known for a long time that the chromophores in the photosynthetic antennae are present at very high number density. More recently, structural studies have discovered an exceptionally high degree of organization, and exquisite and precise placement of Chl molecules relative to each other in many photosynthetic antenna systems [89]. Many Chl molecules are very close together - only approximately 8 – 20 Å between neighboring Chl molecules. The Chl molecules are held at specific relative orientations in large macromolecular complexes. Therefore, we expect a range of interaction energies, ranging from strong to very weak.

Förster's 1965 paper [80] was the first published account relating the different mechanisms of transfer and giving the conditions for each. His analysis was based on the relative magnitude of the coupling energy to the spectroscopic bandwidths. Until now we have discussed the topic mainly from the point of view of time scales. The dynamic characteristics of molecular and spectroscopic processes are directly related to the frequency scale by Fourier transformation, and this leads naturally do a discussion in terms of energy scales. We cannot do justice to Förster's analysis, or to the numerous elegant theoretical analyses that have followed his publication. Selections of more recent references are listed in the following sections (for a few earlier treatments – with references -   see the work of e.g., M. Kasha, R.S. Knox, and R.M. Pearlstein [90-97]). One of the main points in Förster's article was to show that the basic physics of the different energy transfer mechanisms, extending from strong coupling, through weak (sometimes called intermediate) to very weak coupling, are related and can be derived from the same fundamental principles. Förster described the variation in the modes and dynamics of excitation transfer by considering the relationship between, the energies of interaction and the spectral widths of the electronic and vibrational spectral bands [80]. In this paper he distinguished three types of coupling: **strong, weak** and **very weak**. Terminology has been varied throughout the literature, but the following discussion of the three cases will clarify what is meant.

10.1 Very weak coupling

As described above, in the very weak coupling case (that is, the limit of weak coupling, called by some authors as just weak coupling), the transfer of the excitation energy takes place only after the excited donor has become fully vibrationally relaxed. To be precise, the vibrational energy levels in every chromophore are in thermal equilibrium with their molecular environment; that is, the vibrational energy levels are populated according to a Boltzmann distribution. In fact, it has been shown recently that the LH-II exciton system achieves Boltzmann equilibrium in under a picosecond, i.e., much shorter than the typical time scale (5-10 ps) for an exciton to be transfered to a neighboring light-harvesting complex [98]. Due to collisions of the chromophores with their molecular environment, the molecular wave functions on the separate molecules become completely dephased (in general each collision will dephase the molecular wavefunction completely). The well known FRET equations [28, 99-101], are based on Dirac's Fermi Golden Rule, which assumes this complete incoherence. This is the case for most molecular systems in condensed matter (e.g. solutions or biological structures). The intermolecular interactions are Coulombic, as is also the case for excitons. If the molecules are sufficiently far apart, then the coupling can be expressed as an electric dipole-dipole interaction. Since complete vibrational relaxation is assumed, this results in Förster's famous **R^{-6}** equation for FRET [28, 99], with the familiar transition dipole-transition dipole interaction, overlap integral and kappa square (the orientational factor between the transition dipoles). The overlap integral relates the optical spectral overlap between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor, and because the coupling is very weak in FRET, the spectra are identical to that of the individual non-interacting molecules in the same environment (this is an important characteristic of the applicability of FRET). As already mentioned above, in photosynthetic systems, some of the Chl molecules are too close together for the dipole interaction to be strictly valid, because the intermolecular distances are comparable to the size of the molecular transition dipoles. Then the original Förster theory must be extended.

A dominant characteristic of FRET is that the rate of transfer is proportional to the *square* of the interaction energy. This results from the complete incoherent nature of the transfer process. In other words, the transfer dynamics can be modeled as a normal kinetic process. Förster derived a theoretical quantum mechanical description of energy transfer that is valid up to a certain point, which is applicable to both incoherent and coherent transfer (this was the reason he maintained that the fundamental physics was the same). Then he made the following observation. The incremental energy transfer during each small time increment between collisions takes place independently of the previous time increment. This is because each collision destroys all phase relations between all wave functions. So to speak, after each collision, the probability of energy transfer proceeds along the identical time course. Therefore, the probability that the transfer has taken place at a time t can be easily calculated: the quantum mechanical probability of transfer during an average time (using the general expression for this probability) between collisions is multiplied by the time t divided by the average time of a collision τ. The rate of transfer (number of transfers per unit time) is then just this probability (at time t), divided by t, and this turns out to be a time independent rate constant.

Förster's approach emphasizes the difference in FRET and exciton transfer; if the coupling energy is large compared to the width of the vibrational levels, then the transfer would proceed extensively according to the exciton model *before* the next collision (in the limit of large coupling energy the transfer would be completely excitonic). If the width of the vibrational level is large compared to the coupling energy, then the progression between collisions is so small, that the transfer ends up proceeding according to the FRET mechanism. Because in the FRET limit the vibrational relaxation is complete, the energy levels of the excited state are very broad, and therefore the FRET transfer process is moderately slow (nanoseconds) compared to excitonic transfer ($10\text{-}10^3$ femtoseconds). This is because in FRET the spectral widths are broad; the probability is small that the donor and acceptor molecules are simultaneously at identical locations within their spectral bandwidths, which is required to allow energy transfer to take place (electronic transitions of the donor and acceptor must be of equal energy to obey energy conservation). In FRET the excitation energy is said to "hop" from one molecule to the other in a stochastic manner (that is, in a diffusion-like process). In general, the breadth of the electronic absorption and emission spectra are quite broad, and consequently the probability that the donor and acceptor molecules will simultaneously have the same transition energies is small (this is expressed in the overlap integral). This decreases dramatically the rate of energy transfer; of course, this is a direct consequence of the fact that the coupling energy is small compared to the width of the vibrational energy levels. The rate of transfer is proportional to the square of quantum mechanical amplitudes, and there are no quantum interference effects (as there are with excitons, see below). An important characteristic of normal intermolecular FRET is that the excitation energy is completely localized on either the donor or acceptor molecule; thus the total excitation wave function at any time involves only the excited state of either the donor or the acceptor molecules, and the other partner is in the ground state.

10.2 Strong and intermediate (weak) coupling - excitons

The description of excitonic energy transfer is very different from FRET. When the interaction energy (between two molecules of a dimer) is larger than the difference of the energy levels of the two separate non-interacting molecules, the appropriate wave functions of the excited state are the symmetric and anti-symmetric combinations ($\Phi_\pm$) of the locally excited configurations (where the excitation is on one molecule; that is, the excitation is distributed over both molecules). In this case, the energies of these two combination states ($\Phi_\pm$) differ by 2x the coupling energy (2U). This energy difference is the so-called exciton splitting, mentioned above. If there are many coupled molecules, the energy levels are split into many levels, approaching bands when the number of molecules gets very large. But the important point is that due to the coupling, the energy levels of the system changes from those of the individual molecules, and this can be seen from absorption spectrum measurements. For instance, the reaction center dimer, P700, made up of a molecule of Chl a and a molecule of Chl a' , has two bands when oxidized by light, one at ~680 nm, and another at ~700 nm; see e.g. a discussion in chapter 29 of Ke [102]. This is a purely quantum effect with no classical analogy. It arises from mixing the wave functions of the separate monomers (that is, the singly excited product wave functions are summed over all molecules forming the exciton's structure; see the section on "Excitons - a Basic View"). From such measurements excitons can be directly observed from their absorption spectra. The transition dipoles for spectroscopic transitions between the ground state and the excited states of excitons are weighted vector sums of the transition dipoles of the individual molecules. The oscillator strengths of the spectroscopic transitions to the different excitons energy levels depend on the geometry and orientations of the monomers; this provides information about the structures of the exciton aggregates, and on the strength of the coupling.

In excitonic transfer, the rate of energy transfer is directly proportional to the interaction energy, not the square of the coupling energy (as it is for FRET). Since the participating time dependent wave functions all have a complex (meaning a complex number) phase, this leads to the possibility of interference effects and of oscillatory behavior if the molecules retain their phase for a certain time following the excitation. This oscillatory behavior happens whenever quantum amplitudes interfere. This is the origin of the quantum wave behavior of excitons involving aggregates of molecules that are interacting strongly enough so that the wave function of the excited state involves more than just one excited molecule. In effect, the excitation is dispersed (transferred) extremely rapidly (in less than a picosecond) over multiple molecules. This is most easily pictured if one considers the very simplified case of just two interacting molecules with only two states – excited and ground states. Due to the phase coherence between the two molecules, the probability that the excitation can be considered to be at one of the molecules or the other oscillates, and the frequency of this oscillation depends on the coupling energy and the difference in the energy levels of the individual molecules [103]. The time of such oscillations is generally in the femtosecond region. The structure is said to resonate. Thus, the resonant excitonic structure leads to very rapid energy migration among the molecules forming the excitons, as long as the coherence lasts. This is the expected behavior of any quantum system consisting of two interacting structures with only two states. This is the circumstance discussed above in section "Excitons - a Basic View" where we have mentioned the original quantum mechanical treatments of interacting systems by Schrödinger and Heisenberg. The coherent oscillatory behavior and the excitonic splitting (see below) are solely quantum phenomena. Excitons can consist of multiple closely associated, coupled molecules, and similar (but more complex) behavior of coherent wavelike dispersion is expected. However, this is an idealized picture, and assumes that the two molecules (in the case of dimers) are completely separated from the rest of the universe. In actuality, the possibility that this phase coherence will last for a specific time depends on the strength of the interaction with the molecular environment, which leads to rapid de-coherence. This competition between rapid excitonic energy transfer and de-coherence are central to the efficiency with which energy of excitation can be transferred from one position to another by excitonic transfer; for instance, from the location of photon absorption in antenna systems to the reaction center.

A major breakthrough in the quest to see coherence was in the observation of wavelike exciton motion in the Fenna-Mathews-Olson (FMO) antenna from the green bacterium *Chlorobaculum tepidum* at cryogenic temperatures [104]. Further coherent dynamics has been observed in the reaction centers from the purple bacterium *Rhodobacter sphaeroides*, [105], also at low temperatures. Ishizaki and Fleming [88] concluded after a theoretical examination of quantum coherence that it may be present at physiological temperatures for several hundred femtoseconds! Most recently, Robert Alfano (personal communication, January, 2010) demonstrated the existence of coherence in higher plant leaves at room temperature using an elegant and simple experiment measuring the interference from the fluorescence emission during primary photosynthesis. A visibility V = 0.65 was determined from the fluorescence fringes observed at and about 685 nm. This observation suggests the operation of both coherence and incoherent hopping dynamics of the excitation energy transport from photon capture in the antenna to the reaction center.

Several others have discussed in great detail the effects of quantum conversion on photosynthetic excitation energy transfer [106-107].

It is still a matter of great interest and contention in the literature how prevalent and effectual coherent transfer is under normal conditions (normal temperatures) for photosynthesis. Unambiguous evidence for excitonic transfer is found at lower temperatures; however, even there the distance over which energy can migrate by coherent transfer is limited. Such experiments require extremely fast spectroscopic experiments (in femtoseconds) to detect excitonic behavior and sophisticated computation for interpretation in terms of molecular models. Most such experiments on photosynthetic systems have been carried out at low temperatures in order to extend the coherence time. Reviews of such measurements and discussions of the interpretations can be found in recent literature of the different research groups – experimental and theoretical (see further references in sections 11 and 12).

11. MIGRATION, TRANSFER-TO-TRAP, AND TRAPPING

THE QUESTION: WHAT ARE THE LIMITING STEPS?

It is sometimes difficult to calculate and to measure energy migration, but it is clear what is meant by migration of energy within an antennae system, even though it is still unknown how effective exciton transfer is and to what extent it plays a role under normal photosynthesis conditions. However, there are differences of opinion as to what defines the kinetic bottleneck for the excitation energy to enter into the chain of electron

transfer events in the reaction center [95, 108-111]. The question is: Where is the kinetic step located in the chain of events by which the excitation energy is transferred into the electron transfer chain in an irreversible manner (or largely irreversible) - such a step is called "trapping"? A related question is whether there is a single step involved in trapping, or does one have to consider a combination of elementary steps. The "*transfer-to-trap*" step usually refers to the final transfer of energy from the antennae system to the components in the reaction center, which directly precede the initial charge separation. It is well known that the overall electron transport rate is governed not by any of these reactions, but by e.g., diffusion to, and reoxidation of, the reduced plastoquinone (PQH2) by the cytochrome b6f complex; the half-time of this reaction is several ms (see e.g., [112-113]). Further, the overall photosynthetic rate is limited by the enzymatic reaction in the Calvin- Benson carbon fixation cycle at the level of Rubisco (Ribulose bis phosphate carboxylase/oxygenase) (see a review by Von Caemmerer et al. [114]). The question that is pertinent to the mechanism of energy transport in the photosynthetic unit is: Which step(s) limits the overall trapping? Is it the transfer-to-trap step, or the trapping step itself? Obviously the answers depend on the definitions of the different kinetic steps, as well on which kinetic models are used to relate measured kinetic data to derived rate constants. Most researchers define trapping of excitation energy only up to the time that primary charge separation takes place. In our opinion, and those gleaned from the majority of papers, the primary charge separation involving reaction center chlorophylls and pheophytins, is in the range of a few ps (0.3 ps-8ps; see a historical report [115]), but the time of the excitation migration to the unit where charge separation occurs is much longer, e.g., 20-50 ps. Thus, it is generally believed that the system is limited by "transfer-to-the-trap" [116-117]. However, Holzwarth and coworkers [108, 118] argue against this because they include, in PSII trapping, the well-known slower electron transfer step from reduced pheophytin to the first plastoquinone electron acceptor Q_A. It is beyond the purview of this paper to discuss this topic further, but this fundamental question is central to much present research. Trapping is also related to the topic of energy migration in antennae systems. For instance, do quantum wavelike coherent excitonic energy transfer mechanisms in the sub-picosecond range play a critical role in the functioning of biological systems? Or is the rate of excitation transfer via a hopping mechanism (FRET) between individual pigments sufficient? These are intriguing and difficult questions. The answers very probably depend on the type of photosynthetic system under investigation. A general view is that within several antenna complexes (e.g., FMO; and B800), there may very well be CRET, but from one antenna complex to another (and to the reaction center), it may be FRET. Then again, within the reaction centers there may be CRET as well as FRET, justifying, in a general way, the title of our paper "*From FRET to CRET and Back*".

12. LEVELS AND DEVILS OF COMPUTATION

The descriptions of the interactions in the pigment-protein complexes of a photosynthetic system are much more complex than we have described above. The level of the interactions and the structures vary greatly also within any photosynthetic system. The parameters such as the excitonic couplings, the coupling to the vibrations of the environment of the chromophores, site energies and the time scales of relaxation all affect the rate of energy transfer, and can even possibly affect the pathway. In this paper we have been concerned mainly with a simple, fundamental description of the theoretical background. However, it is clear that for a real photosynthetic system the distances between the chromophores participating in energy transfer vary extensively, as do the couplings between the chromophores and between the chromophores and the environment. The recent explosion in structural information has initiated an extensive theoretical and computational literature. The various theories can be somewhat subdivided depending on the relative strengths of the interactions between chromophores and the structural geometries. Rather than listing and choosing among the numerous references for this difficult advanced theoretical and computational subject, we refer to a few reviews and papers, from which the reader can obtain the original and later references [21, 87-88, 109, 119-130]. We provide below brief descriptions of some of the major theoretical approaches being discussed in the literature.

12.1   Förster's very weak coupling theory

If the coupling is very weak, then the excitation energy transfer takes place between excited and ground states that are localized on the different individual pigments. This leads to a hopping mechanism (described by a random walk probability-based mechanism) as described above, and the rate of transfer is proportional to the square of the Coulomb coupling, which in Förster's original treatment is transition-dipole transition-dipole coupling.

12.2 Redfield theory

Redfield theory is used for the case of strong excitonic coupling and weak exciton-vibrational coupling. The rate constant for exciton relaxation between excitonic delocalized states is described in terms of the coefficients in the summation of the molecular product wave functions that make up the exciton wave functions (remember there are N different energy levels for N participating molecules making up the excitons). The rate constant for this transition is proportional to a sum (over all pairs of molecules) of negative exponentials that are functions of the distance between the different chromophores (this is an approximation and is the corresponding electronic overlap factor); each member of the sum is weighted by the product of the coefficients of the molecular wave functions in each excitons state. Also involved in this rate constant is a factor representing the efficiency by which energy can be exchanged between the proteins and the chromophores. The reorganizational energy is the coupling to the local protein vibrations. It is an integral over the spectral density, weighted by the frequency; the spectral density is the weighted density of states of the protein vibrations coupling to the local transitions of the pigments. If the reorganizational energy is large compared to the intermolecular coupling, then Förster's FRET theory is applicable.

12.3 The modified Redfield theory

The modified Redfield theory was developed to study strong exciton-vibrational coupling as well as strong excitonic coupling. The goal is to take both couplings into account without invoking perturbation; the modified Redfield theory includes the nuclear reorganizational effects when considering the interaction between deolocalized states. Because the electric density is different for the different excitonic states, the nuclei relax toward the new equilibrium positions; therefore, for strong excitonic-vibrational coupling it is necessary to take the exciton-vibrational coupling into account. This is done by treating the diagonal elements of the excitonic-vibrational coupling to describe the reorganizational effects; the normal Redfield theory neglects this. If all these diagonal strong exciton-vibrational coupling is neglected, the standard Redfield theory results. A rate constant for the modified Redfield theory was first given by Mukamel and coworkers (see Zhang et al. [131]) and the name modified Redfield theory was introduced by Yang and Fleming [129].

12.4 The generalized Förster theory

The generalized Förster theory is applied to systems of weakly coupled domains of delocalized states, where the delocalized states are made of strongly coupled pigments. Either the Redfield theory or the modified Redford theory may be necessary to describe the relaxation within the domains. The Förster theory is invoked to take into account the transfer of the excitation energy from the excitonic state of one domain to a neighboring domain. The Förster theory is extended to take into account the pairwise interaction of pigments from each domain, the contribution of each pair is weighted by the coefficients of the contribution of each pigment to the state of each corresponding exciton domain. These pairwise contributions are then summed. If the two domains are far enough apart compared to their spatial extensions, then one can use effective average transition dipoles of the domains in the Förster theory. Otherwise, if the aggregates (domains) are closer, each pair of pigments must be taken into account. It is difficult to take into account both the excitonic and excitonic-vibrational couplings in the domains when calculating the absorbance and fluorescence line shape functions needed for the inter-domain Förster calculation.

12.5 Reconciling dissipative quantum mechanics methods with Förster theory

The approximations inherent in Förster and (modified) Redfield theories prevent either from being universally applicable to all light-harvesting systems In an effort of conciliation, there is a recent rise in the development and use of dissipative quantum mechanics methods that aim to directly compute the time evolution of the density matrix using a hierarchy method [132-133]. This approach has been applied recently to exciton systems in the FMO complex in green sulfur bacteria [88] and the LH-II complex in purple bacteria [98].

As the computational cost of the aforementioned hierarchy method rises nearly exponentially with the number of pigments involved, it is currently not possible to study systems containing more than a few dozen pigments. Notably,

generalized Förster theory is shown to give similar results to the hierarchy method for energy transfer between a pair LH-II complexes.

Thermal disorder presents a constant challenge for the study of light-harvesting proteins and their quantum biology. Thermal effects can be viewed in terms of a dynamic disorder model involving trajectory averages [122], or a static disorder model involving ensemble averages in the context of random matrix theory [134]. Photosynthetic organisms seem to have evolved to not only cope with, but to exploit the effects of thermal disorder for efficient light-harvesting function.

12.6 System level view of energy transfer: from individual proteins to entire organelles

Both in bacteria and plants, light harvesting is performed by assemblies of hundreds of cooperating proteins. Despite decades of data on the structure and function of individual constituent proteins, the global architecture of the photosynthetic units both in oxygenic and anoxygenic systems still contain many unknowns. Recently, Atomic Force Microscopy (AFM) studies of photosynthetic membranes in purple bacteria revealed the spatial organization of the light-harvesting proteins within the membrane [135-136].

Fig. 2. Structural model of a chromatophore vesicle of the purple bacterium *Rhodobacter sphaeroides*. Shown is the protein arrangement containing 101 LH-II complexes surrounding 18 dimers of LH-I reaction center complexes, containing approximately 4000 bacterio-chlophylls [137]. Proteins are shown as semi-transparent on the right hand side to display the bacteriochlorophyll network. Constituting light-harvesting proteins are shown to be excitonically coupled to one another resulting in uniformly high quantum efficiency at room temperature. Notably absent from the model shown are the cytochrome bc1 complex and ATP-synthase as current AFM data does not reveal their locations [137].

An *in silico* reconstruction of a chromatophore vesicle based on this AFM data combined with crystallography, Electron Microscopy (EM), and spectral studies revealed a functional view of the complete bacterial unit involved in photosynthesis in atomic details [137] (see Fig. 2). Energy transfer in an entire chromatophore has been described in the context of generalized Förster theory, revealing the basis of efficient light-harvesting across a network of 4000 bacteriochlorophylls distributed over hundreds of proteins that span across 80 nm. Future system level studies of efficient energy harvesting is desperately dependent on methods such as AFM and cryo-EM tomography revealing the global architecture of the light harvesting systems in purple bacteria as well as thylakoids.
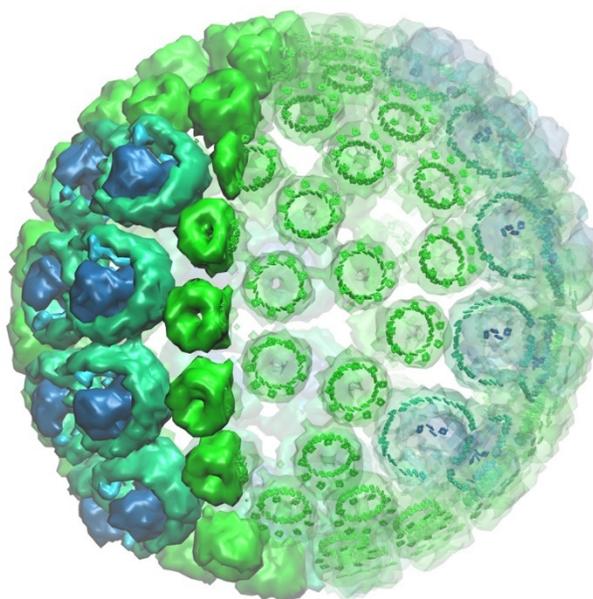
13. POSTSCRIPT.

A very large body of research is available to answer questions dealing with the transfer of energy from the antenna complexes to reaction centers, where the energy is utilized to make life possible. The complexity of the photosynthetic systems has forced experimenters to concentrate on specific biological systems, and often to carry out experiments on separated functional components. The methods of investigation and the conditions of the experiments of the different research groups are often significantly different and hard to compare. The theoretical descriptions have advanced to the stage where it is difficult for the uninitiated to understand in detail, and the terminologies are often not consistent. There are major disagreements among the experts that are difficult to decipher, but seem to instigate lively arguments. Of course, this is a consequence of the difficulty, complexity and the intricacy of the subject, which demands high sophistication of both the experimental and theoretical approaches to the subject. In addition each photosynthetic system possesses distinctive characteristics; experiments carried out in different temporal and spatial regions, and on

samples that differ in their preparation and degree of subunit assembly, are not always easy to compare. This complexity can lead to specialization in the methods of investigation, computation and interpretation, and considering the variety of photosynthetic systems there is probably not a single *modus operandi* for investigating or interpreting the results of experiments for all systems. Nevertheless, it is important to identify the common elements, and to avoid confusing terminology. It is also critical to recognize, and keep in the forefront, the basic physics that underlies all the advanced experiments and sophisticated theoretical and computational approaches. Exactly these many intricate facets of photosynthetic systems are a stimulating test confronting investigators, challenging them to untangle a highly sophisticated, intricate and highly dynamic biological system.

The subtitle of this paper, "*A wheen o' mickles mak's a muckle*", should now be understandable. All the separate parts of the photosynthetic cycle, the mickles, operate synergistically to produce a whole, functionally, highly efficient biological system, the muckle. Even though it is necessary to focus on specific parts of the total mechanism in our experimenting and theorizing, we have to be careful not to extrapolate our interpretations beyond the realm of usefulness and biological effectiveness for the overall efficiency of the entire system. There is still a lot to do.

We end this overview with a photograph of Robert Alfano (the chairperson) and the three speakers (Govindjee; Graham Fleming; and Mohan Sarovar) at the SPIE session on January 27, 2010, held in San Francisco, California; it dealt with topic of coherent and hopping modes of excitation energy transport in photosynthetic systems.
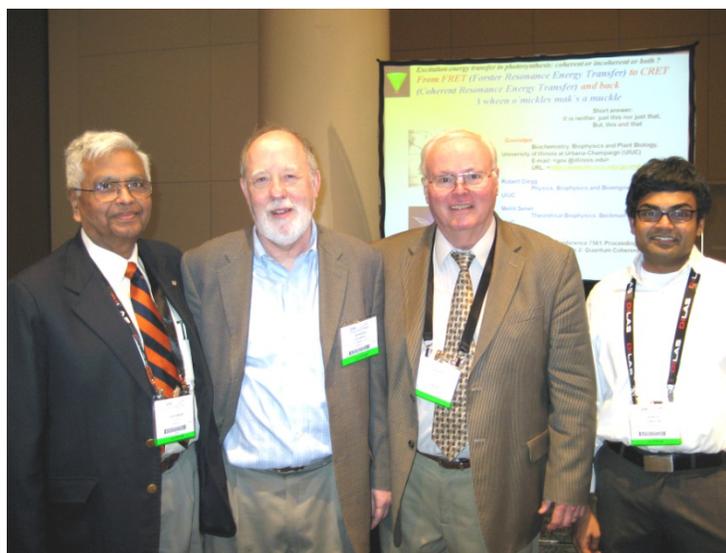
Fig. 3. Left to right: Govindjee (University of Illinois at Urbana-Champaign), Graham Fleming (University of California at Berkeley), Robert Alfano (City University of New York), and Mohan Sarovar (University of California at Berkeley). Photo by Rajni Govindjee.

14. ACKNOWLEDGMENTS

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