

Nonlinearities in Energy Harvesting Media

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ABSTRACT

Both in natural photosynthetic systems and also their molecularly engineered mimics, energy is generally transferred to the sites of its chemical storage from other sites of primary optical excitation. This migration process generally entails a number of steps, frequently involving intermediary chromophore units, with each step characterised by high efficiency and rapidity. Energy thereby accrues at reaction centres where its chemical storage occurs. At high levels of irradiation, energy harvesting materials can exhibit novel forms of optical nonlinearity. Such behaviour is associated with the direct pooling of excitation energy, enabling secondary acceptors to undergo transitions to states whose energy equals that of two or more input photons, subject to decay losses. Observations of this kind have now been made on a variety of materials, ranging from photoactive dyes, through fullerene derivatives, to lanthanide doped crystals. Recently developed theory has established the underlying principles and links between the modes of operation of these systems. Key factors include the chromophore layout and geometry, electronic structure and optical selection rules. Mesoscopic symmetry, especially in photosynthetic pigment arrays and also in their dendrimeric mimics, is here linked to the transient establishment of excitons. The involvement of excitons in energy harvesting is nonetheless substantially compromised by local disorder. The interplay of these factors in photoactive materials design is discussed in the context of new materials for operation with intense laser light.

Keywords: nonlinear optics, energy harvesting, resonance energy transfer, multiphoton, lasers

1 INTRODUCTION: ENERGY TRANSFER IN MULTICHROMOPHORE ARRAYS

The harvesting of light quanta by antenna systems in nature is instrumental in the majority of life cycles on earth. In photosynthetic systems photons are collected by light-harvesting complexes, a variety of which have been resolved in recent years.¹ The transferral of the harvested energy to chemical storage sites, from the locale of primary optical excitation, is well known to be mediated by the process of resonance energy transfer (RET). For a number of years, interest has been focussing on RET processes within molecularly engineered photosynthetic mimics. Such mimics invariably comprise chromophores arrays with the simplest, namely those containing just two chromophoric centres, being the first to be linked with RET studies and subsequently the subject of a number of reviews.²⁻⁴ In these cases one chromophore is considered to be a pre-excited donor with the other acting as an amenable acceptor. Although there are numerous ways for an excited donor to relax in bichromophoric molecules³ (excimer and exciplex formation, intramolecular photochemical reactions, intramolecular electron transfer) interest here focuses upon resonance energy transfer between chromophores. Importantly the task of ascertaining chromophore separations is well-suited to the techniques used and data produced in RET studies, particularly in connection with the technique of fluorescence resonance energy transfer (FRET).⁵

Bichromophoric systems prove to be instrumental in understanding the more complex multichromophore arrays as many of the techniques used to analyse their properties are also relevant when considering more extended systems. Major attention has been given to the role of the structural link between donor and acceptor, commonly termed the *bridge* or *spacer*.⁴ By implementing theory first formulated by Förster,⁶ much research has revolved around the determination of interchromophore distances. Indeed Förster theory has been specifically extended to account for observations in systems containing two *identical* chromophores (donor-donor energy migration or DDEM).⁷ Other investigations, dating from the 1960's⁸ right up to the present day,⁹ have been executed for rigid bridge systems. A more bountiful route however is provided by systems which have a flexible link between donor and acceptor. In this area information has been ascertained about novel transfer systems,^{10,11} the distribution of interchromophore distances in various situations,^{12,13} the effects of spacer length,¹⁴ the nature of like and unlike chromophores,¹⁵ and orientation factors.^{7,12,16} In particular the work of Valeur and colleagues affords a vast source of material.

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Building upon the bichromophore groundwork, investigation in the 1990's have widened to include trimeric systems,^{17,18} photoactive molecular wires,¹⁹ and multichromophore arrays themselves. The latter not only provide the best environs in which to observe the optical nonlinearities under discussion here, but also represents an important area in which much synthetic effort is directed towards the production of efficient mimics of the photosynthetic light harvesting centre. The work of a variety of groups has been implemented in a significant recent success.²⁰ In this context, the nature and evolution of single excitations within large molecular arrays is of great interest and has been elucidated for a variety of systems. Berberan-Santos and co-workers have directed their efforts toward understanding multichromophore cyclodextrins,²¹ whilst more widespread effort has been expended on multiporphyrin arrays,²²⁻²⁴ as in the synthetic photosystem.²⁰

No discussion in this area would be complete without mentioning dendrimers. These highly branched, regularly built macromolecules provide further examples of systems comprising linked chromophores.²⁵ Experimental evidence suggests that any excitations present within the dendrimeric infrastructure are localised to the chromophores themselves and not delocalised over the whole macromolecule.^{26,27} Bearing this in mind, much interest has focused upon intramolecular energy transfer between the constituent chromophores.²⁸ Indeed dendrimers display a variety of photophysical effects indicative of RET including photoisomerisation,^{29,30} light harvesting,^{31,32} and directed energy transfer or funnelling.^{27,33}

In all the commonly studied situations cited above, each and every fundamental energy transfer step takes place between one donor and one acceptor. The theory behind this pairwise energy migration, in systems accountable to post-overlap distance regimes, has been rigorously covered in the past and serves simple situations well.³⁴ However recent work has revealed that bridging species may play a far less passive role, significantly modifying the transfer process.³⁵ In such cases, it is no longer adequate to model the process as simply a donor/acceptor interaction, as the electronic influence of the bridging species has to be properly accounted for.^{36,37} Furthermore, in multichromophore arrays subjected to high levels of laser illumination (specifically those associated with the onset of optical nonlinearity) two or more electronic excitations are likely to coexist locally, facilitating novel energy transfer processes. If decay lifetimes are sufficiently long and the energy levels of chromophores present in the array or molecule are amenable to acquisition of the multi-excitations, such situations will arise even at comparatively modest intensities. It is in these instances that conventional energy transfer theory cannot be used to explain and predict photophysical responses. Recently the theory of the case where two excitations are simultaneously present within the array has been exhaustively studied (*vide infra*) and led to the present study of higher order analogues.

2 THREE-CENTRE ENERGY TRANSFER

At the high levels of laser illumination associated with the onset of optical nonlinearity, the probability that two or more electronic excitations can locally coexist in an array of chromophores becomes a significant consideration. Consider that also present in the vicinity are acceptors whose energy levels are amenable to acquisition of the dual excitations *via* a novel energy transfer process. This has been termed *three-centre energy pooling*³⁸ and later *three-centre energy transfer*.³⁹⁻⁴¹ In various chemical disciplines examples of this type of energy transfer are evident. Interestingly the architectural and photophysical properties of many supermolecular dendrimers, multichromophore arrays, and ionic lattices lend themselves to the exhibition of this novel process. Here, and in the following, 'centre' is a generic term for the donors and acceptors — either distinct molecules, chromophores, or ions. Such three-centre energy transfer interactions can be described in simple terms by the pseudo-chemical equation;



with A and B being donor species (sometimes, but not always, chemically identical), C the acceptor, and an asterisk indicating the site(s) of electronic excitation. It is important to recognise that the total energy transferred to the acceptor is less than or equal to the sum of *initial* excitations of both donors, any losses being due to initial vibronic relaxation of the excited donor states. Also it is necessary to stipulate that neither A or B has an upper level suitable to accommodate the combined energy of the excitations of both, to obviate two-photon absorption processes of either donor.

Due to its ultrafast nature, three-centre energy transfer supports the existence and interplay of two different mechanistic pathways, or quantum channels, termed *cooperative* and *accretive*, as illustrated in figure 1. In particular, the cooperative channel is concerned with direct pooling of donor excitation at the acceptor; accretive channelling is the specific process whereby the excitation of one donor is fleetingly accrued by the second before net transfer to the acceptor. The latter allows two possibilities (as in the outer paths of figure 1).

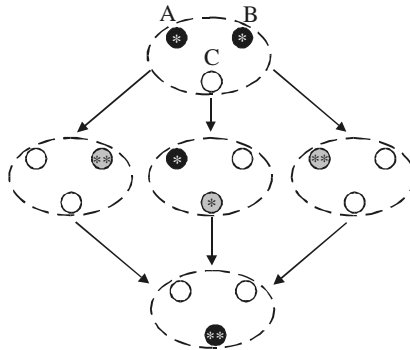


Figure 1: Cartoon to show the different quantum channels of three-centre energy pooling from the initial state (top) to the final state (bottom). The central pathway depicts cooperative transfer with the left and right routes representing the two analogous accretive mechanisms. Black circles represent species in an excited state; white circles show species in the ground state; grey circles are short-lived, energy non-conserving, intermediate states, with asterisks indicating positions of excitation.

Identification of the cooperative and accretive mechanisms widens the theoretical scope of this work. For example, three-centre energy transfer offers all the advantages commonly associated with conventional, unimolecular two-photon absorption at C, with the additional possibility of exploiting the intrinsic dependence on the mutual orientation of the donors and the acceptor. Also it is only the acceptor, not the site of pre-excitation, that needs to exhibit a two-photon absorption cross-section. In other words the initial excitation can be achieved through laser irradiation on a frequency associated with conventional single-photon absorption, giving a high population of excited state donors. Compared to the probability of two excitation photons being absorbed directly by an acceptor, there is generally a greater chance of two photons being captured by any two separate donors in its vicinity, even though both processes have an overall quadratic dependence on the pump laser intensity. Furthermore, in this sense, the three-centre process carries an obvious advantage over two-photon FRET, in which two-photon absorption at a *single* site is followed by energy transfer to a nearby fluorophore. Dual excitation delivery to a single acceptor site is not unlike two-photon FRET — the fundamental difference between the two is that in the latter, a *single* energy transfer step is responsible for deposition of the two-photon excitation energy of a *single* donor.

There are several reasons for the interest in the process described above. One is that it signifies the prototypical example of potentially multi-centre energy transfer processes, conceivably with several tributaries (pre-excited donors) feeding a single reservoir (acceptor). Any such process affords a means of promoting the acceptor site to a state higher in energy than any individual initially excited donor. Secondly, the concerted transfer of excitation energy from two or more donors can circumvent the need, which would otherwise arise in a multi-step process, for suitably placed intermediate energy levels of the acceptor. Thirdly, the cooperative/accretive approach to transfer lends itself well to analysis of the intricacies of some common facets of three-centre energy transfer processes.

For any given system the total three-centre energy migration rate derived from all transfer pathways, Γ^{TOT} , may be determined from Fermi's Golden Rule;

$$\Gamma^{\text{TOT}} = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho \quad (2)$$

where ρ is the density of final states for the acceptor and M_{fi} is the total quantum amplitude for the process, expressible as a sum of contributions from each of the quantum channels thus;

$$M_{fi} = M_{fi}^{\text{coop}} + M_{fi}^{\text{acc1}} + M_{fi}^{\text{acc2}} \quad . \quad (3)$$

Using methods previously expounded,⁴¹ short-range results (for inter-species distances between 10Å and 100Å) for the cooperative and accretive interactions are given by;

$$M_{fi}^{\text{coop}} = \frac{1}{n^4} \left(\frac{n^2 + 2}{3} \right)^4 \frac{|\mu^{0\alpha(A)}| |\mu^{0\beta(B)}| |\alpha^{\gamma0(C)}| \kappa_{AC} \kappa_{BC}}{(4\pi\epsilon_0 R^3)(4\pi\epsilon_0 R'^3)} \quad , \quad (4)$$

$$M_{fi}^{\text{acc1}} = \frac{1}{n^4} \left(\frac{n^2 + 2}{3} \right)^4 \frac{|\mu^{0\alpha(A)}| |\mu^{\gamma0(C)}| |\alpha^{0\beta(B)}| \kappa_{BC} \kappa_{AB}}{(4\pi\epsilon_0 R'^3)(4\pi\epsilon_0 R'^3)} \quad , \quad (5)$$

and;

$$M_{fi}^{\text{acc2}} = \frac{1}{n^4} \left(\frac{n^2 + 2}{3} \right)^4 \frac{|\mu^{0\beta(B)}| |\mu^{\gamma0(C)}| |\alpha^{0\alpha(A)}| \kappa_{AC} \kappa_{AB}}{(4\pi\epsilon_0 R^3)(4\pi\epsilon_0 R'^3)} \quad . \quad (6)$$

Notation introduced in equations (4-6) includes the transition dipole moment of each chromophore ξ defined by $\mu^{fi(\xi)} = \langle f | \mu^{(\xi)} | i \rangle$ where i and f indicate the initial and final molecular system states respectively (0 — the ground state, Greek letters — an excited state); intermolecular vectors $\mathbf{R} = \mathbf{R}_C - \mathbf{R}_A$, $\mathbf{R}' = \mathbf{R}_C - \mathbf{R}_B$ and $\mathbf{R}'' = \mathbf{R}_B - \mathbf{R}_A$; the refractive index of the intervening medium n ;⁴²⁻⁴⁴ and the two-photon interaction tensor, $\alpha^{fi(\xi)}(\omega_i, \omega_f)$, whose generalised form is given by;⁴⁵

$$\alpha_{ij}^{fi(\xi)}(\mp \omega_i, \mp \omega_f) = \sum_{\zeta} \left\{ \frac{\mu_i^{f\zeta(\xi)} \mu_j^{\zeta i(\xi)}}{(E_{i\zeta}^{\xi} \pm \hbar \omega_i)} + \frac{\mu_j^{f\zeta(\xi)} \mu_i^{\zeta i(\xi)}}{(E_{i\zeta}^{\xi} \pm \hbar \omega_f)} \right\} \quad . \quad (7)$$

In (7) the energy difference terminology $E_{ij}^{\xi} = E_i^{\xi} - E_f^{\xi}$ is introduced and ζ represents any one of all the molecular states of ξ . For the cooperative quantum channel described by equation (4), the two-photon interaction tensor (7) exhibits an index-symmetric form analogous to that governing a (single-beam) two-photon process. Conversely, for the accretive mechanisms of equations (5) and (6) equation (7) shares the same non-symmetric form as the tensor which supports all forms of electronic Raman scattering.⁴⁶ The cooperative mechanism has a distinct advantage over conventional two-photon absorption at the acceptor, being subject to different selection rules. The photon flux needed to doubly excite a single molecule may be of a similar order to that required to excite two donors sufficiently close to the acceptor (to initiate the cooperative mechanism) but the relative longevity of singly (compared to doubly) excited sites proves to be a deciding factor. The different roles of this tensor reflect the different ways for energy transfer to be effected. The scattering-like behaviour in accretive mechanisms owes its origin to the excitation at either donor being passed on to the acceptor, *via* a second donor as a mediator to the process, whereas the cooperative mechanism may be thought of as simple, mediation-free, dual interaction at C.

An important facet of the results contained within equations (4-6) is the identification of features akin to the well-known orientational factor κ which itself plays an important role in predicting the behaviour in conventional pairwise energy transfer systems.⁴⁷ As this discussion concerns three-centre energy transfer the exact form of the parameters differs slightly from the traditional κ . As such, subscripts are introduced to define the various interchromophore displacements. Explicitly;

$$\kappa_{AC} = \cos \Theta_{AC} - 3 \cos \phi_A \cos \phi_C \quad (8)$$

$$\kappa_{BC} = \cos \Theta_{BC} - 3 \cos \theta_B \cos \theta_C \quad (9)$$

$$\kappa_{AB} = \cos \Theta_{AB} - 3 \cos \gamma_A \cos \gamma_B \quad (10)$$

introducing a variety of angles given by;

- ϕ_ξ — the angle between μ_ξ and $\hat{\mathbf{R}}$
- θ_ξ — the angle between μ_ξ and $\hat{\mathbf{R}}'$
- γ_ξ — the angle between μ_ξ and $\hat{\mathbf{R}}''$
- $\Theta_{\xi\xi'}$ — the angle between μ_ξ and $\mu_{\xi'}$.

The adoption of such an approach, essentially reducing the analysis to a trigonometric problem, proves highly profitable for the fruitful analysis of several situations discussed in the following sub-section.

2.1. The Case of the Equilateral Triangle

In order to further the understanding of multitributary energy transfer processes it is helpful to scrutinise some specific chromophore geometries. Previously a linear wire containing two donors and a single acceptor has been studied using the appropriate trigonometry⁴⁰ and optimum configurations identified for the mutual donor and acceptor orientations. Here it is pertinent to consider the case of a chromophore triad forming an equilateral triangle array shown in figure 2.

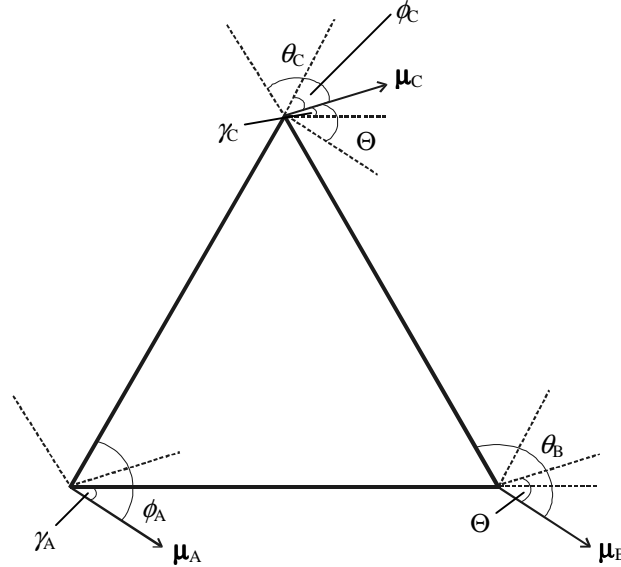


Figure 2: Definition of angular variables for a three-centre system configured as an equilateral triangle. Due to the parallel and coplanar nature of the donor transition dipoles, not all angles are shown explicitly.

As in reference 40, however, it is necessary to impose certain restrictions on the array in order to produce data which proves useful. Consider that the array is coplanar with the transition dipoles of each chromophore, also that both donors are

electronically and chemically identical, and that donor transition dipoles are parallel implying $\Theta_{AB} = 0$ and $\Theta_{AC} = \Theta_{BC} = (\Theta)$. To fully describe the mutual orientation of all the vectors in a free triad fifteen angles are required however, taking into account the restrictions imposed, this number is drastically reduced. The internal angles all equal $\pi/3$, and, using previous results,⁴⁰ it may be shown that;

$$\cos \gamma_{\xi} = \cos \phi_{\xi} - \cos \theta_{\xi} \quad . \quad (11)$$

From figure 2 it may also be deduced that, in general we have $\gamma_{\xi} = \phi_{\xi} - \pi/3$, and $\theta_{\xi} = \phi_{\xi} + \pi/3$ with specifically $\phi_A = \phi_B$, $\theta_A = \theta_B$, and also $\gamma_A = \gamma_B$. In order to visualise the rate variation associated with the relative orientation of the acceptor transition dipole μ_C with respect to the parallel donor transition moments, let Θ signify the angle between them (defined in a clockwise sense) such that;

$$\phi_C = \phi_A + \Theta \quad . \quad (12)$$

Using the above relation, the results provided by equations (4-6) may be re-written in terms of two key variables, the angles ϕ_A and Θ ;

$$M_{ji}^{\text{coop}} = m_1 (\cos \Theta - 3 \cos \phi_A \cos(\phi_A + \Theta)) (\cos \Theta - 3 \cos(\phi_A + \pi/3) \cos(\phi_A + \Theta + \pi/3)) \quad , \quad (13)$$

$$M_{ji}^{\text{acc1}} = m_2 (\cos \Theta - 3 \cos \phi_A \cos(\phi_A + \Theta)) (1 - 3 \cos^2(\phi_A - \pi/3)) \quad , \quad (14)$$

and;

$$M_{ji}^{\text{acc2}} = m_2 (1 - 3 \cos^2(\phi_A - \pi/3)) (\cos \Theta - 3 \cos(\phi_A + \pi/3) \cos(\phi_A + \Theta + \pi/3)) \quad . \quad (15)$$

where the constants m_1 and m_2 entail molecular and interspecies parameters and may for present purposes be considered roughly equivalent. By insertion of (13-14) into equation (2) the dependence of the rate Γ with angles ϕ_A and Θ may be ascertained. Thus;

$$\Gamma \propto f(\phi_A, \Theta)^2 \quad (16)$$

where;

$$f(\phi_A, \Theta) = (\cos \Theta - 3 \cos \phi_A \cos(\phi_A + \Theta)) (\cos \Theta - 3 \cos(\phi_A + \pi/3) \cos(\phi_A + \Theta + \pi/3)) \\ + (2 \cos \Theta - 3 \cos \phi_A \cos(\phi_A + \Theta) - 3 \cos(\phi_A + \pi/3) \cos(\phi_A + \Theta + \pi/3)) (1 - 3 \cos^2(\phi_A - \pi/3)) \quad , \quad (17)$$

providing the functional form depicted in figure 3. Taking slices through the three-dimensional surface plot of figure 3a at fixed values of the angle Θ offers insight into certain configurations of the equilateral triangle of figure 2 with varying values of ϕ_A . Possibly the most interesting feature of figure 3 relates to the case where all the transition dipoles are parallel ($\Theta = 0$). Here, the function f takes a constant value (225/256), no matter what the value of ϕ_A . The angle-independence of the result in this special case reflects the threefold symmetry of the array transition moments under these conditions. Some further salient features of figure 3 are highlighted in figure 4, in which a number of other interesting features are evident. For example it is apparent that configurations where the transition dipoles are anti-parallel yield the most favourable conditions for three-centre energy transfer, with orthogonal cases also yielding a fairly significant contribution.

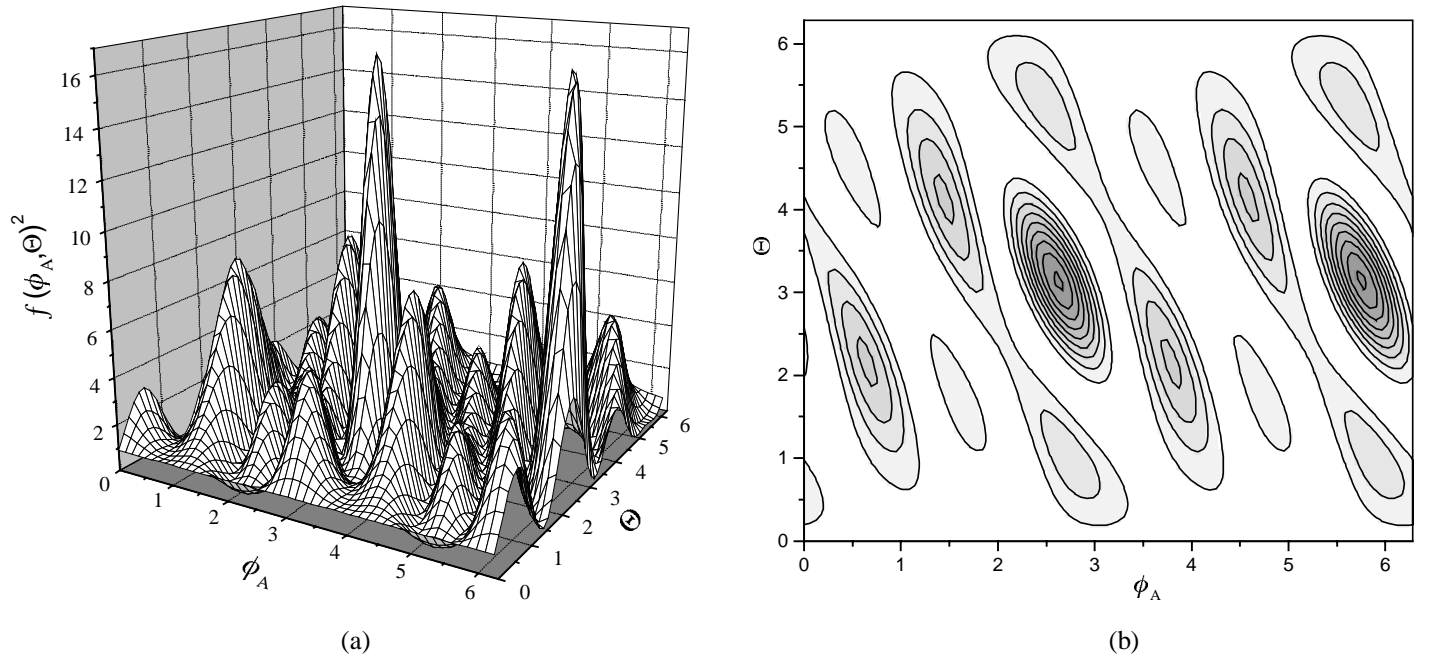


Figure 3: Plots illustrating how the rate of three-centre energy transfer in an equilateral array varies with angles ϕ_A and Θ : (a) 3D graph. (b) contour map – vertical scale arbitrary.

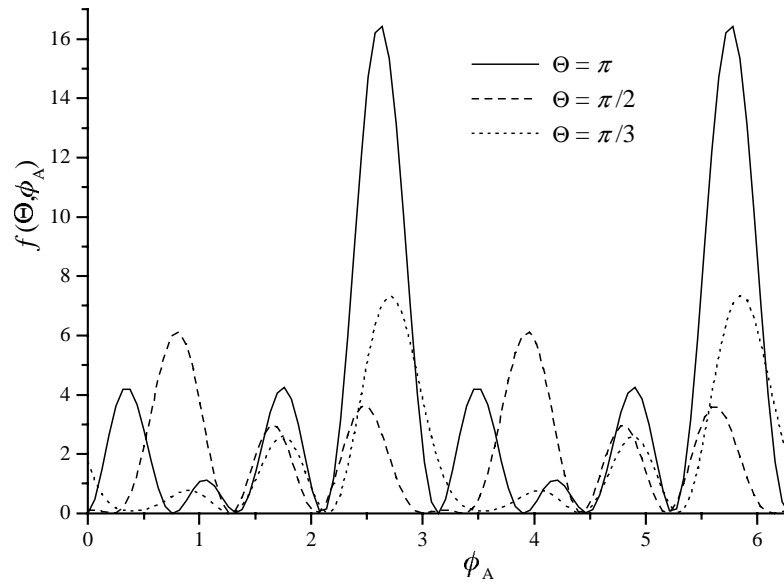


Figure 4: Slices through figure 3(a) illuminating fixed angles between transition dipoles of π , $\pi/2$, and $\pi/3$ (see graph for key).

3 DISCUSSION: FOUR-CENTRE SYSTEMS

As shown in section 2, the simple addition of an extra species into an energy transfer process increases the complexity of the problem substantially. However if an accurate theory is to be formulated for excitation movement in light harvesting systems, accommodating nonlinear effects multi-centre transfer must be properly understood. To this end exciton propagation must also be brought into its proper context. Consider a four-species array comprising three suitable donor chromophores and an acceptor (as shown in figure 5). Such configurations are common in dendrimeric systems with the dendrites (A) funnelling excitation energy to the central trap (B).

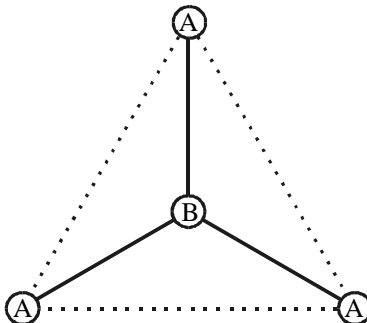


Figure 5: Four-species array showing three chemically identical donors (A) and one acceptor (B).

Interest here centres on the photophysics of energy migration within such a system. On passage of an intense laser beam through such an array, a number of absorptions may occur at the donors (dependent on energy levels within the chromophores and the beam frequency). Ultimately, as a result of energy transfer processes yet to be characterised (work in progress), this leads to excitation of the central trap and relaxation of the donor(s). In general the overall process may be described by;



with the excitation uncertainty (the delocalised exciton) represented by the bracketed donor species in the second stage. The exciton can be thought of comprising quantum superposition of three distinctly localised excitations. A trivial case where any one of the three single donors is excited (leading to three permutations of the excitation localisation) and conventional RET is responsible for the excitation of B is possible. Secondly, three-centre energy transfer theory (outlined in section 2) can account for cases where two donors are excited. Thirdly, theory describing novel four-centre energy transfer processes is required to account for the situation where all three donors are initially excited. Within these three umbrella processes there are a variety of mechanisms by which transfer occurs, for example the cooperative and accretive mechanisms highlighted in section 2 may be thought of as distinct mechanisms of the overall three-centre energy transfer. Table 1 shows salient properties of the excitation.

| No. Excited Donors | Migration process | Localisation Permutations | Mechanisms |
|--------------------|------------------------------|---------------------------|------------|
| 1 | RET | 3 | 1 |
| 2 | Three-Centre Energy Transfer | 3 | 3 |
| 3 | Four-Centre Energy Transfer | 1 | 16 |

Table 1: Features of excitation transfer channels within a four centre array.

Work currently being undertaken within this group aims to clarify the interplay between the three migration process and hence provide insight into excitonic behaviour in chemical analogues. Before this can be done the intricacies of four-centre energy transfer must be addressed. With three-centre energy transfer the contributions of the cooperative and accretive quantum channels to the overall quantum amplitude (2) and their relative importance are well understood.^{38-41,46} In order to appraise similarly the contributions to the overall quantum amplitude of four-centre energy transfer the salient mechanism must be identified and quantified. The sixteen mechanisms fall into four categories shown in figure 6.

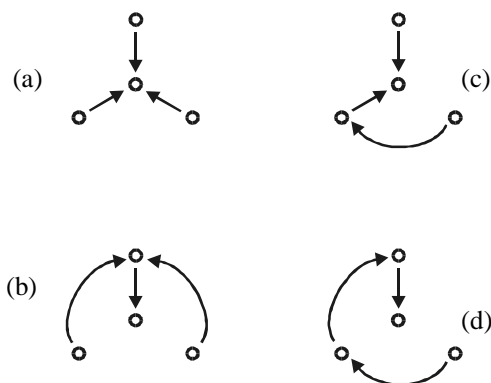


Figure6: Cartoons describing the four basic categories of mechanism for of four-centre energy transfer. Arrangement as in figure 5.

Figure 6 (a) represents the only four-centre energy process of its type and can be thought of as being analogous to cooperative three-centre energy transfer. Inspection reveals that the quantum amplitude will depend upon the cube of the transition dipole of A (μ^A) coupled with a three-photon tensor associated with B (β^B). The mechanism embodied in 6(b) is one of 3 such channels proportional to $(\mu^A)^2 \mu^B \beta^A$. The remaining two sub-processes each exemplify one of six pathways for four-centre energy transfer exhibiting transition dipole moments and two-photon interaction tensors similar to (7). Figures 6(c) and 6(d) signify quantum channels with amplitudes proportional to $(\mu^A)^2 \alpha^A \alpha^B$ and $\mu^A \mu^B (\alpha^A)^2$ respectively. The exact calculation of each quantum amplitude, along with the significance of their interplay with other migration process, is the main objective of ongoing work.

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