

## Excitons

“We can think of a line of identical *neutral* atoms one of which has been put into an excited state- that is, with more than its normal ground state energy. Let  $C_n$  be the amplitude that the  $n$ th atom has the excitation. It can interact with neighboring atom by handing over its extra energy and returning to the ground state.... Now the object which moves is called an *exciton*. It behaves like a neutral ‘particle’ moving through the crystal carrying the excitation energy” – The Feynman lectures on physics, III p. 13-9.

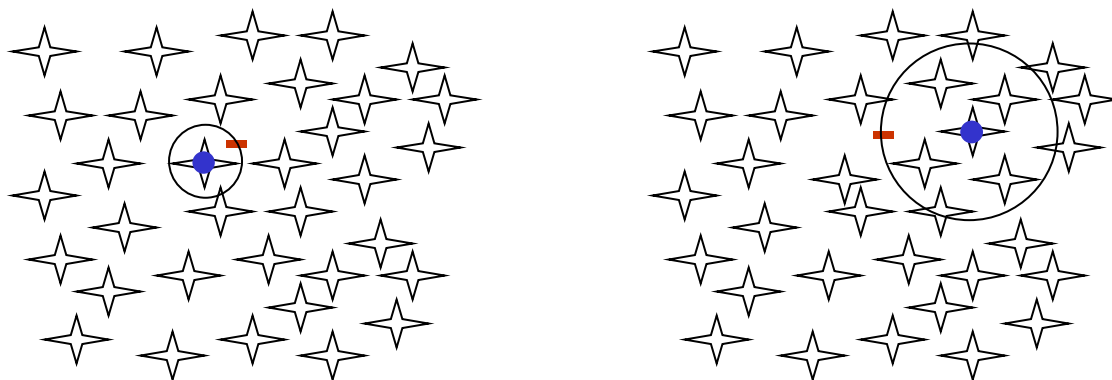
In our case we are not concerned with individual atoms but rather with molecules but one can still adopt the general description of a neutral excitation that can move between molecules. In this kind of description we think of a neutral [molecular] state just as we may consider a negatively-charged or positively-charged state.

Things may become a bit complicated when one try to impose concepts derived from specialised fields<sup>1)</sup>. To farther describe the exciton we can ask ourselves several questions as: a) Can we describe the exciton as a combination of an electron and a hole. b) If “a” is true, to allow for the pair to move as an entity (prerequisite of an exciton) do the particles have to be mutually confined in space. c) If “a” is true, to allow for the pair to move as an entity does there have to be a spin correlation? Commonly, all the above questions are answered by a YES and, at this stage, we will take it to be true. The last and sometimes confusing issue<sup>1)</sup> is related to another question one may ask: d) If “a” and "b" are true does the coulomb attraction must play a significant role? (unfortunately I have no intentions to try and answer it at this stage).

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<sup>1)</sup> See lecture on Charge Excitation and the comment on pg. 8

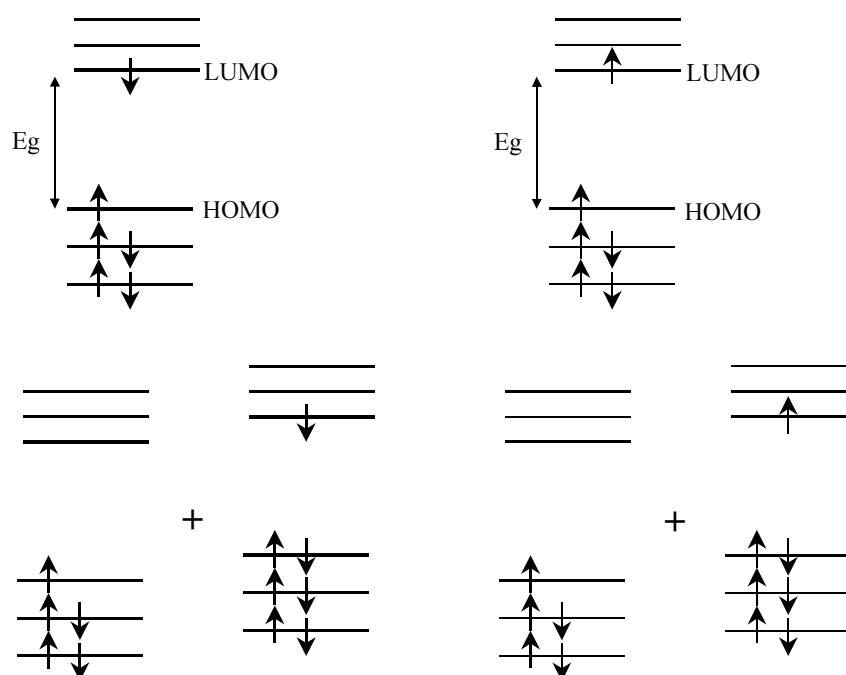
### Frenkel and Wannier Excitons



**Figure 1. The spatial discrimination of exciton types. The Frenkel exciton is localised on or around a molecule (site) and the Wannier exciton is more extended.**

Figure 1 shows schematically the separation of the exciton into two spatial types. The Frenkel exciton is highly localised and is often found in molecular solids where the molecules are not densely packed. When the medium is dense (like in crystals) then the atoms screen some of the e-h attraction and the exciton size spread into larger space. These are called Wannier excitons.

We can classify excitons in another way and that is according to their spin or their optical activity (see more discussion in singlet-triplet below).



**Figure 2. Schematic description of the exciton as being the sum of an electron and a hole state. Note that the relevant spin states.**

In the current picture there is a correlation between the lower and upper electronic state and we can now consider two exciton states (Figure 2). One where the electron in the upper state has the same spin as the vacant electron in the lower state. And second where the electron in the upper state has an opposite spin. The relaxation of the second case (right) requires a spin flip (momentum) and is not optically active. The existence of these two types of excitons is very important also from a practical point of view. If we consider that charge injection into light-emitting diodes has no spin correlation then the total efficiency may be limited due to carriers being “lost” to form the non-emissive triplet exciton. Using this motivation we add a bit more background below.

### Singlet - Triplet

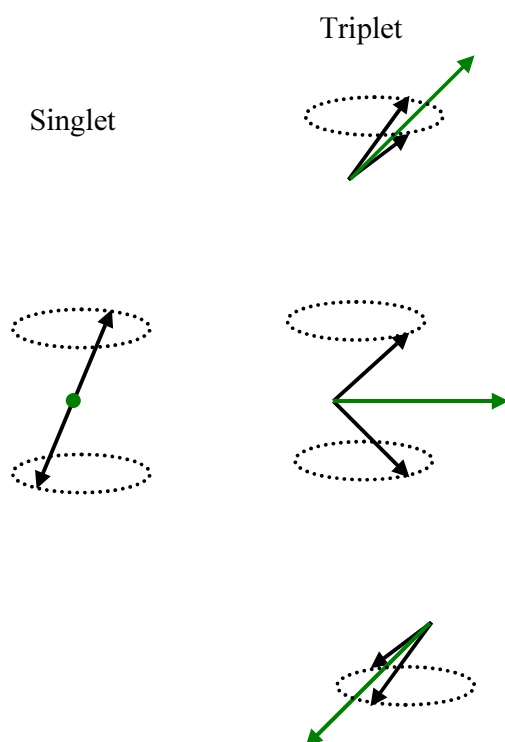
Prior to excitation, the Pauli exclusion principle states that two electrons occupying the same orbital must be ‘paired’ – that is, they must have opposite spins. After excitation the two electrons may have either paired or parallel spins, since they now occupy different orbitals. To fully understand the nature of the triplet state and how it may be reached in electronic spectroscopy, the electrons of the system must be considered. An electron may be viewed as an electrically charged particle which generates a magnetic angular momentum as a result of its spin. This angular momentum

is termed electronic spin,  $S$ , and represented as a vector. This electronic spin must precess about an axis so that the uncertainty principle is not violated, and this axis will be the direction of the strongest magnetic field that the electron experiences. Quantum mechanics requires that  $S$  is quantised, and as such, only two measurable orientations of the spin are allowed to occur, so the electron may be described as either 'spin up' or 'spin down' with respect to the  $z$ -axis.

Consider a two-spin system described by  $\psi_i\psi_j$ , with associated spins of  $S_i$  and  $S_j$ . The two spins may not only be either spin up or down, but may also precess either *in* or *out* of phase. If *in* phase, the two spins will always point in the same direction. If *out* of phase, they will always point in opposite directions in the  $xy$ -plane. This provides *four* possible spin vector representations to characterise the two-spin system (see Figure 3). The spin quantum number,  $S$ , may be either 0 or 1. If zero, there is only one possibility for the magnetic quantum number,  $M$  ( $M=0$ ), and the  $S=0$  state is therefore called the 'singlet' state. If  $S=1$ , there are three possible integer values for  $M$  (1, 0, -1), giving rise to three degenerate states, known collectively as the 'triplet' state. These configurations may be visualised by considering the precession of the component spins:

- (a) Both  $i$  and  $j$  are 'spin up', to give a resultant spin vector ( $S=1$ ), and a magnetic moment ( $M=1$ ).
- (b) Both  $i$  and  $j$  are 'spin down', giving a resultant spin vector ( $S=1$ ), and a magnetic moment ( $M=-1$ ). Both (a) and (b) are triplet configurations, since  $S=1$  in both cases.
- (c) One spin is 'up' (arbitrarily chosen) and one is 'down' with respect to the  $z$ -axis, so there is no resultant magnetic moment ( $M=0$ ). However, this may still be a triplet configuration if the spin vectors are precessing in-phase, which results in a spin vector perpendicular to the  $z$ -axis ( $S=1$ ).
- (d) If, as in (c), there is one spin 'up' and one 'down' ( $M=0$ ), but the spin vectors are precessing out of phase, such that they are in opposite directions, no overall spin vector exists ( $S=0$ ), and a singlet state results.

The three triplet configurations are effectively degenerate, but will be separated in energy in a magnetic field.

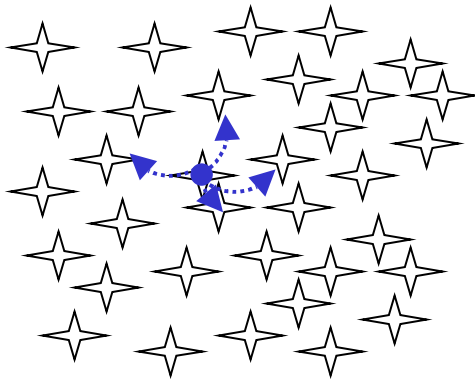


**Figure 3. A vector based picture of the singlet (left) and triplet (right) spin configurations.**

In the triplet state, the Pauli exclusion principle operates to make the two parallel spins avoid one another more effectively than in the singlet state where the spins are paired. This increased avoidance minimises electron-electron repulsions and causes the triplet state of any particular energy level to be stabilised with respect to the corresponding singlet state by a quantity known as the *exchange energy*.

Going into the exact description of the excitons on a polymer chain is beyond this lecture however the motion of these excitons is the essence of there being. In the following we will only make use that the singlet is optically active and that the triplet is not.

### Transfer Mechanisms



**Figure 4. Schematic description of the exciton as a moving excitation.**

Figure 4 describes schematically an excited site that can transfer its energy (the exciton) to various other sites in the bulk around it. We discuss below three forms of energy transfer mechanisms Trivial, Förster, and Dexter.

#### Trivial transfer:

Emission  $\rightarrow$  absorption

Effective for  $R > 10\text{nm}$  and is a two step process

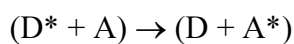


To be effective:

1. Quantum efficiency of D (donor) is high
2. Many (high density) of A (acceptor) molecules in the path
3. High extinction (absorption) coefficient of A
4. Spectral overlap between emission of D and absorption of A.

$$J \equiv \int_0^{\infty} \overline{I_D} \overline{\varepsilon_A} d\nu; \overline{I_D} \text{ and } \overline{\varepsilon_A} \text{ are normalised } \int_0^{\infty} \overline{I_D} \overline{I_D} d\nu = 1; \int_0^{\infty} \overline{\varepsilon_A} \overline{\varepsilon_A} d\nu = 1.$$

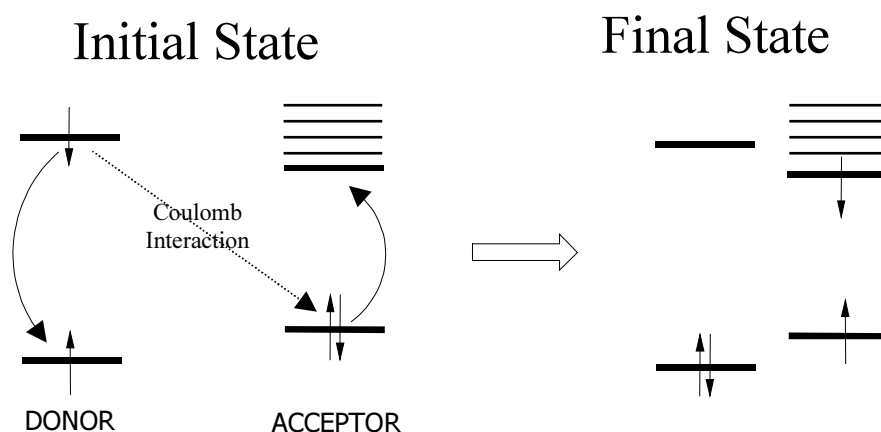
#### Radiationless



$$\text{Rate, Probability} \sim \langle \text{initial state} | \text{coupling} | \text{final state} \rangle^2 = \langle \Psi_i | H | \Psi_f \rangle^2$$

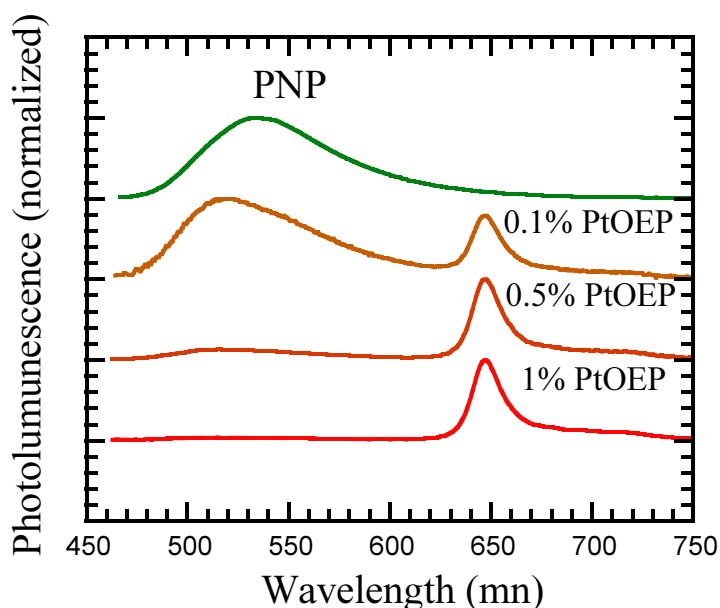
### Förster (singlet) transfer

Another well documented transfer mechanism is that first discussed by Förster. This mechanism describes a radiationless transfer process, which therefore does not involve emission of the light from the donor molecule at any stage. It proceeds instead via a coulombic interaction of the dipoles of the two molecules,  $D^*$  and A. The movement of the excited electron on the donor molecule creates an oscillating dipole, which in turn induces an alternating electric field. This oscillating electric field induces a dipole in the acceptor molecule. For to be efficient the oscillating electric field needs to be in resonance with an electron in the acceptor molecule. In this case there will be efficient coupling via dipole-dipole interaction and, possibly resulting in promotion of the electron to an excited state on A, and de-excitation of the electron on D.



**Figure 5. Schematic description of Förster transfer.**

Unlike the trivial transfer the Förster transfer is an effective decay channel for the D molecule and it modifies the lifetime of D. For example, if the D molecule has a non-radiative channel competing with its radiative channel it is possible to bypass the non-radiative channel by transferring the energy fast to A which can be chosen to be an efficient emitter. Figure 5 also suggests that this could be an efficient colour-tuning scheme (see Figure 6).



**Figure 6. The effect of gradually adding acceptor molecules (red) to a donor polymer host (green).**

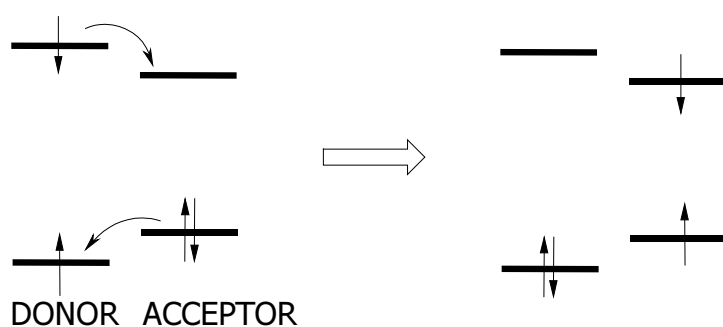
Förster was the first to suggest that resonance conditions are related to the emission and absorption spectrum overlap. Since the inducing field varies as  $R^{-3}$  the induced dipole varies also as  $R^{-3}$  and hence the dipole-dipole interaction varies as  $R^{-6}$ .

$$k_{ET}(\text{dipole} - \text{dipole}) = \left( \frac{1}{\tau_D} \right) \left( \frac{R_0}{R} \right)^6$$

### Dexter (Triplet or Singlet) Transfer

The third and final energy transfer mechanism to be discussed here is Dexter energy transfer. The interaction here is of a collision type and it requires a spatial overlap between the electronic wavefunction in D and A. This mechanism is an electron exchange (tunnelling) process, where the excited electron from the donor molecule is exchanged for a ground-state electron from the acceptor molecule. The two exchanges may either occur simultaneously, or one after another. If it is a stepwise process, charged species will be generated after step one.



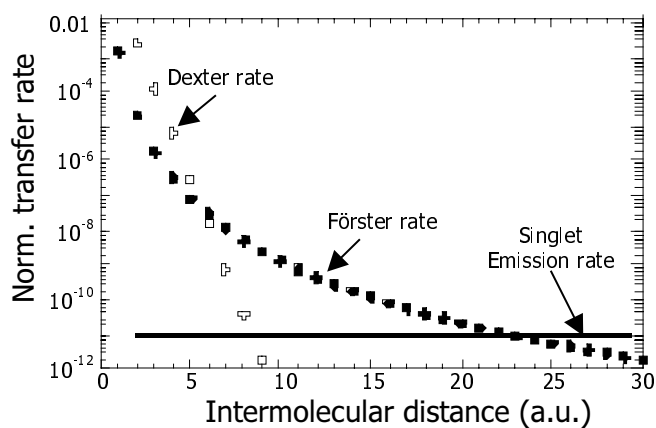


**Figure 7. Diagrammatic representation of triplet-triplet (Dexter) energy transfer.**

Since Dexter energy transfer involves the overlap of electrons (wavefunction), the electronic spin is inconsequential and the mechanism may also operate for formally spin-forbidden transfers between triplet states. The rate of the transfer via this mechanism is also exponentially dependent on the distance between the donor and acceptor molecules, as would be expected for a tunnelling mechanism. The rate constant for Dexter transfer is therefore:

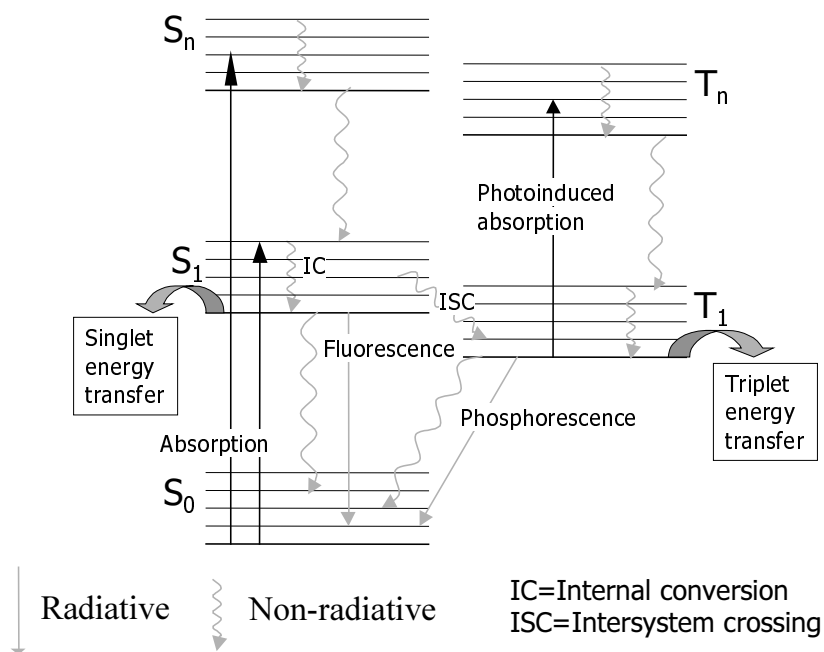
$$k_{ET}(\text{exchange}) = KJ \exp\left(-\frac{2R_{DA}}{L}\right)$$

where  $K$  is related to the specific orbital interactions,  $J$  is a spectral overlap integral normalised for the extinction coefficient of the acceptor, and  $R_{DA}$  is the distance between donor and acceptor relative to their van der Waals radii,  $L$ . This mechanism is therefore very sensitive to the distances between molecules, the rate of transfer decreasing exponentially as the donor and acceptor are moved apart. The greater effect of the distance between the molecules on the rate of Dexter transfer as compared with Förster transfer is both intuitive once the nature of the transfer mechanisms is known, and reflected in the rate equations for the two processes. The rate of Dexter transfer shows an exponential dependence on the intermolecular distance, whilst Förster transfer displays a  $1/R^6$  dependence on the same factor. The relative dependence of Förster and Dexter transfer on the spatial proximity of the molecules involved is shown in Figure 8.



**Figure 8. Relative distance dependence of Förster and Dexter transfer**

The summary of the mechanisms found on a single electronic-unit (molecule or conjugation length) is shown in Figure 9



**Figure 9. The dynamical processes found within the singlet and triplet manifolds of a single molecule.**

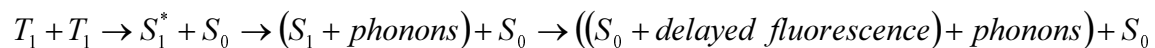
Since excitons are mobile (by definition) and assuming we might want to extract some of their properties (as in an experiment) → we outline some of the reactions excitons may go through:

### Singlet-Singlet

1.  $S_1 + S_1 \rightarrow S_1^* + S_0 \rightarrow (S_1 + \text{phonons}) + S_0 \rightarrow ((S_0 + \text{fluorescence}) + \text{phonons}) + S_0$
2.  $S_1 + S_1 \rightarrow e + h + S_0$  - auto-ionisation
3.  $S_1 + S_0 \rightarrow T_1^* + T_1^*$  - fission

We remember that the likelihood of a process may change between polymers and, among other things, it depends on the relative energy levels of initial and final states.

### Triplet-Triplet



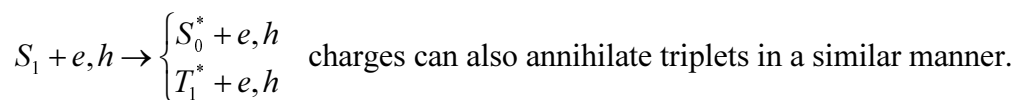
This is called delayed fluorescence since triplets (which have long lifetime) may collide and generate singlets long after the singlet population has decayed.

$T_1 + T_1 \rightarrow (T_1^* \text{ or } T_2) + S_0 \rightarrow (T_1 + \text{phonons}) + S_0$  and will generally end as phonons or very weak phosphorescence.

### Traps

If there are traps in the system then there could be interactions between free and trapped species (for both singlet and triplet).

### Exciton-Charge



### Exciton-Surface

1. Charge transfer to trapping centre at the interface (oxygen = electron trap).
2. Energy transfer molecule on the surface

### Metals

1. Polarise the molecules next to it (as in mirror image effects) and change the electronic (position of) states. This may cause the surface molecules to act like traps.
2. Energy transfer to the metal

I would like to thank V. Cleave for allowing parts of her PhD thesis (text and figures) to be used in this lecture.

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