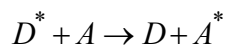
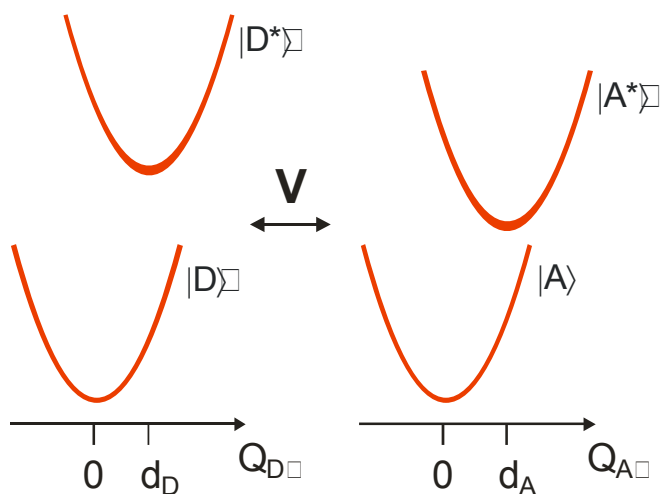


## Förster Energy Transfer

Nonradiative transfer of electronic excitation from a donor molecule to an acceptor molecule:



The transfer arises from dipole-dipole coupling, but does not involve a light field. In general, there are four states to worry about:



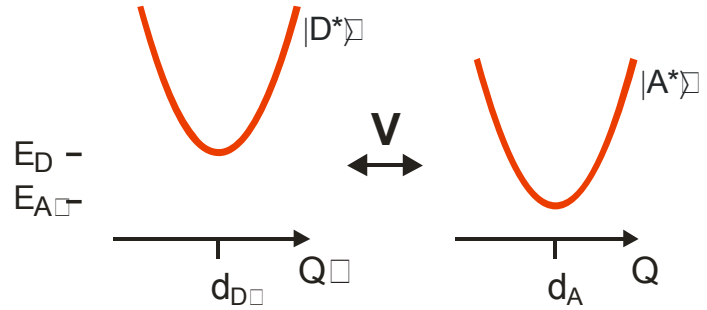
Let's just consider the case where we have already excited the donor electronic transition, and the acceptor is in the ground state. We will state that the system can only exist either with the donor excited and acceptor in the ground state, or vice-versa. If the system is weakly coupled through a dipole-dipole interaction, we can write:

$$H = H_0 + V$$

$$H_0 = |D^*A\rangle H_D \langle D^*A| + |A^*D\rangle H_A \langle A^*D|$$

$$H_D = \frac{p^2}{2m} + m \omega^2 (Q - d_D)^2 + E_D$$

$$H_A = \frac{p^2}{2m} + m \omega^2 (Q - d_A)^2 + E_A$$



(Here  $|D^* A\rangle$  represents the electronic and nuclear states for both donor and acceptor molecules, which could be more properly written  $|D^* n_{D^*} A n_A\rangle$ ).

The interaction between donor and acceptor takes the form of a dipole-dipole interaction:

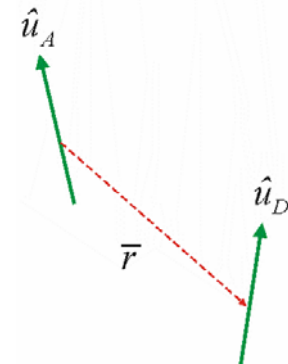
$$V = \frac{3(\bar{\mu}_A \cdot \hat{r})(\bar{\mu}_D \cdot \hat{r}) - \bar{\mu}_A \cdot \bar{\mu}_D}{\bar{r}^3}$$

where  $r$  is the distance between donor and acceptor molecules, and the dipole operators are

$$\bar{\mu}_A = |A\rangle \bar{\mu}_{AA^*} \langle A^*| + |A^*\rangle \bar{\mu}_{A^*A} \langle A|$$

$$\bar{\mu}_D = |D\rangle \bar{\mu}_{DD^*} \langle D^*| + |D^*\rangle \bar{\mu}_{D^*D} \langle D|$$

For the dipole moment, we can factor out the orientational contribution as a unit vector, i.e.,



$$\bar{\mu}_A = \hat{u}_A \mu_A$$

where  $\mu_A$  is the dipole operator. This allows us to write:

$$V = \mu_A \mu_B \frac{K}{r^3} \left[ |D^* A\rangle \langle A^* D| + |A^* D\rangle \langle D^* A| \right]$$

All of the orientational factors are now in the term  $K$ :

$$K = 3(\hat{u}_A \cdot \hat{r})(\hat{u}_D \cdot \hat{r}) - \hat{u}_A \cdot \hat{u}_D$$

Now we can write the rates of transition from Fermi's Golden Rule:

$$w_{k\ell} = \frac{2\pi}{\hbar^2} |V_{k\ell}|^2 \delta(\omega_k - \omega_\ell)$$

where the initial state  $\ell = |D^* A\rangle$  and the final state  $k = |A^* D\rangle$ .

We also know we can express Fermi's Golden Rule as a correlation function in the interaction Hamiltonian:

$$\langle w_{k\ell} \rangle = \frac{2\pi}{\hbar^2} \sum_{\ell} P_{\ell} |V_{k\ell}|^2 \delta(\omega_k - \omega_{\ell}) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle$$

Note that this is not a Fourier transform!

Substituting, we find

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{K^2}{r^6} \langle D^* A | \mu_D(t) \mu_A(t) \mu_D(0) \mu_A(0) | D^* A \rangle$$

where  $\mu_D(t) = e^{+iH_D t} \mu_D e^{-iH_D t}$ .

We have also neglected rotational motion of the dipoles. Most generally,

$$K^2 = \langle K(t) K(0) \rangle$$

but this factor is easier to evaluate if the dipoles are static, or they rapidly rotate to become isotropically distributed. For the static case  $K^2 = \langle K^2 \rangle = 0.475$  and for the fast reorientation

$$K^2 \rightarrow \langle K(t) \rangle \langle K(0) \rangle = \langle K \rangle^2 = 2/3.$$

Since the dipole operators act only on  $|A\rangle$  or  $|D^*\rangle$ , and the  $D$  and  $A$  nuclear coordinates are orthogonal,

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{K^2}{r^6} \underbrace{\langle D^* | \mu_D(t) \mu_D(D) | D^* \rangle}_{\text{Donor Fluorescence } C_{D^*D^*}(t)} \underbrace{\langle A(t) | \mu_A(t) \mu_A(D) | A \rangle}_{\text{Acceptor Absorption } C_{AA}(t)}$$

Remember  $|D^*\rangle$  represents the electronic and nuclear configuration  $|D^* n_{D^*}\rangle$

$$C_{D^*D^*} = |\mu_{DD^*}|^2 e^{-i(\omega_{DD^*} - 2\lambda_D)t - g_D^*(t)}$$

$$C_{AA} = |\mu_{AA^*}|^2 e^{-i\omega_{AA^*}t - g_A(t)}$$

The expression for  $w_{ET}$  is a time integral over a product of correlation functions. Since we can express the T.C.F.s as inverse F.T.s over lineshapes:

$$C_{D^*D^*}(t) = \int_{-\infty}^{+\infty} d\omega e^{i\omega t} \sigma_{fluor}^D(\omega)$$

$$C_{AA}(t) = \int_{-\infty}^{+\infty} d\omega e^{i\omega t} \sigma_{abs}^A(\omega)$$

We can express the energy transfer rate as an overlap integral between the donor fluorescence and acceptor absorption spectra:

$$w_{ET} = \frac{1}{\hbar^2} \frac{K^2}{r^6} |\mu_{DD^*}|^2 |\mu_{AA^*}|^2 \int_{-\infty}^{+\infty} d\omega \sigma_{abs}^A(\omega) \sigma_{fluor}^D(\omega)$$

(Here  $\sigma$  is the lineshape normalized to  $|\mu|^2$ .) So the energy transfer rate scales inversely with  $r^6$ , depends on the strengths of the electronic transitions for donor and acceptor molecules, and requires resonance between donor fluorescence and acceptor absorption. The rate of energy transfer is usually written in terms of an effective distance  $R_0$ , and the fluorescence lifetime of the donor:

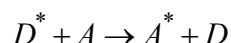
$$w_{ET} = \frac{1}{\tau_{fluor}} \left( \frac{R_0}{r} \right)^6$$

At the critical transfer distance  $R_0$ , defined by the overlap integral above, the rate (or probability) of energy transfer is equal to the rate of fluorescence.

## Marcus Theory\*

Electron transfer for weakly coupled donor and acceptor states, i.e., non-adiabatic E.T.

This closely follows the formulation of energy transfer where



now represents the transfer of an electron. The difference in this case is that the nuclear coordinate mediates the electron transfer.

Normally we associate the rates of electron transfer with the free-energy along the electron transfer coordinate  $Q$ , but here we will start just by writing the transfer rates in terms of the potential energy as before:

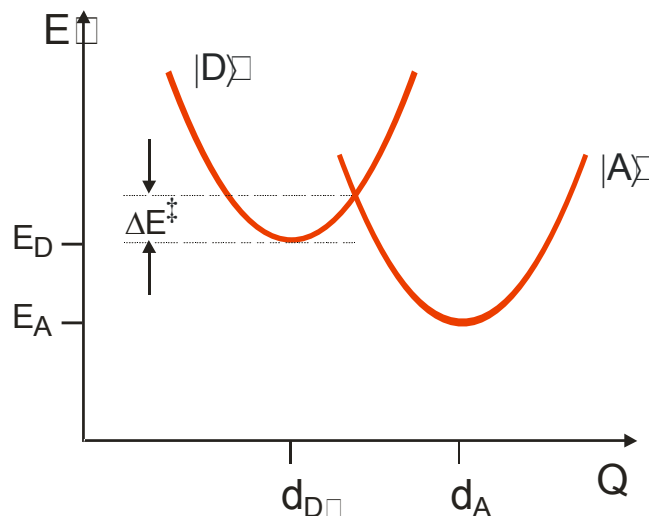
$$H = H_0 + V$$

$$H_0 = |D\rangle H_D \langle D| + |A\rangle H_A \langle A|$$

$$H_D = E_D + \left( \frac{p^2}{2m} + \frac{1}{2} m \omega^2 (Q - d_D)^2 \right)$$

$$H_A = E_A + \left( \frac{p^2}{2m} + \frac{1}{2} m \omega^2 (Q - d_A)^2 \right)$$

$$V = J [ |D\rangle \langle A| + c.c. ]$$



where  $J = J_0 \exp\left(\frac{-\beta}{2}(R - R_0)\right)$  is the electronic coupling matrix element, which drops off exponentially with the separation between donor and acceptor orbitals. The operator acts only on the electronic states

\* See P. F. Barbara, T. J. Meyer, and M. A. Ratner, "Contemporary issues in electron transfer research." J. Phys. Chem. **100**, 13148-13168 (1996), and references within.

For a number of coupled nuclear coordinates,  $Q_\alpha$  :

$$g(t) = \sum_{\alpha} d_{\alpha}^2 \left[ (\bar{n} + 1)(e^{-i\omega_{\alpha}t} - 1) + \bar{n}(e^{+i\omega_{\alpha}t} - 1) \right]$$

Substituting into F.G.R., we find the rate of electron transfer is:

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{-i(E_D - E_A)t} \exp \left[ \sum_{\alpha} \left( \frac{d_{\alpha}^A - d_{\alpha}^D}{2} \right)^2 \left( (n_{\alpha} + 1)(e^{-i\omega_{\alpha}t} + 1) + \bar{n}(e^{+i\omega_{\alpha}t} - 1) \right) \right]$$

If, as before, we do a short-time expansion of the exponential:

$$w_{ET} = \frac{J^2}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{-i(E_D - E_A - \lambda)t} \exp \left( - \sum_{\alpha} \left( \frac{d_{\alpha}^A - d_{\alpha}^D}{2} \right)^2 \omega_{\alpha}^2 (2\bar{n}_{\alpha} + 1)t^2 \right)$$

$$\propto \exp \left[ \frac{-(E_D - E_A - \lambda)^2}{4\lambda kT} \right]$$

where  $\lambda = \sum_{\alpha} \hbar \omega_{\alpha} \left( \frac{d_{\alpha}^A - d_{\alpha}^D}{2} \right)^2$ .

Note that  $-\Delta E^{\ddagger} = E_D - E_A - \lambda$  .