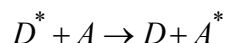


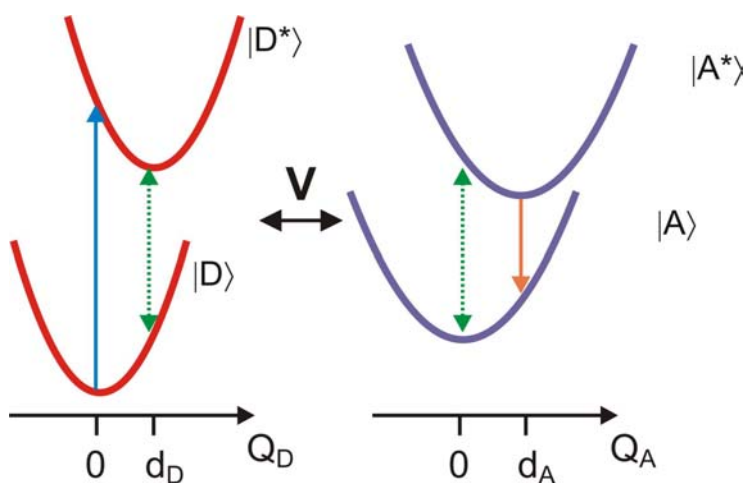
MIT Department of Chemistry
 5.74, Spring 2005: Introductory Quantum Mechanics II
 Instructor: Professor Andrei Tokmakoff

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:

$$H = H_0 + V$$

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

Here H_D is the Hamiltonian of the system with the donor excited, and H_A is the Hamiltonian with the acceptor excited. $|D^*A\rangle$ represents the electronic and nuclear states for both donor and acceptor molecules, which could be more properly written $|d^*n_D, an_A\rangle$.

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. The dipole operators here are more properly referred to as the transition dipole moments that couple the ground and excited electronic states for the donor and acceptor:

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

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

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 μ_A is the dipole operator. The coupling, a transition dipole interaction, can now be written as:

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

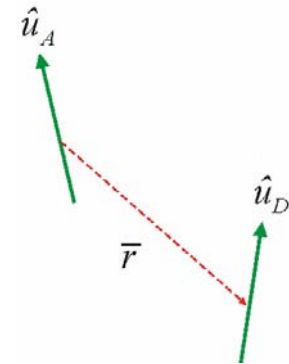
All of the orientational factors are now in the term K :

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

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:

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

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

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,

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{K^2}{r^6} \underbrace{\langle D^* | \mu_D(t) \mu_D(0) | D^* \rangle}_{\text{Donor fluorescence } C_{D^*D^*}(t)} \underbrace{\langle A | \mu_A(t) \mu_A(0) | A \rangle}_{\text{Acceptor absorption } C_{AA}(t)}$$

Remember $|D^*\rangle$ represents the electronic and nuclear configuration $|d^* n_{D^*}\rangle$. As before, we can write the correlation functions for the donor emission and acceptor absorption as

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

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

where we have made use of $\omega_{D^*D} = \omega_{DD^*} - 2\lambda_D$, which expresses the emission frequency as a frequency shift of 2λ relative to the donor absorption frequency.

The expression for w_{ET} is a time integral over a product of correlation functions. Since we can express the time-correlation functions as inverse Fourier transforms 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 σ 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:

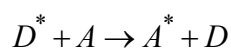
$$w_{ET} = \frac{1}{\tau_{fluor}} \left(\frac{R_0}{r} \right)^6$$

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:

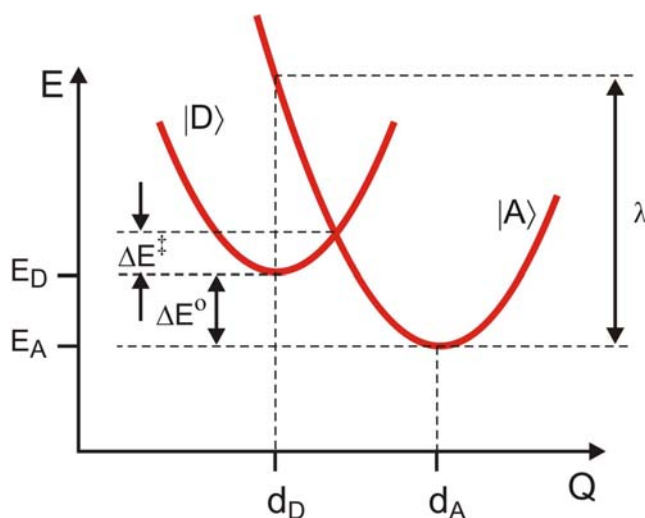
$$H = H_0 + V$$

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

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

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

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



where $J = J_0 \exp(-\beta(R - R_0))$ 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. Also, J. Jortner, "The temperature dependent activation energy for electron transfer between biological molecules." *J. Chem. Phys.* **64**, 4860-4867 (1976).

We can proceed to calculate the rates of electron transfer from the Golden Rule expression

$$\begin{aligned} w_{k\ell} &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle \\ &= \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{-i(E_A - E_D)t/\hbar} \langle e^{iH_D t/\hbar} e^{-iH_A t/\hbar} \rangle \end{aligned}$$

For a sum of many coupled nuclear coordinates, Q_α :

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

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

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

A more explicit evaluation of this vibronically mediated transfer rate is given in Jortner.

To get a feeling for what this behavior is like, we can do a short-time expansion of the exponential:

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

In the high temperature limit ($kT \gg \hbar\omega$) we get

$$w_{ET} \propto |J|^2 \sqrt{\frac{1}{\lambda kT}} \exp \left[\frac{-(E_D - E_A - \lambda)^2}{4\lambda kT} \right]$$

where $\lambda = \sum_{\alpha} \hbar\omega_{\alpha} (d_{\alpha}^A - d_{\alpha}^D)^2$. Note that $-\Delta E^{\ddagger} = E_D - E_A - \lambda$.

This is equivalent to Marcus' result for the Arrhenius rate, in which we associate the potential energy with the free energy for the electron transfer reaction:

$$k_{ET} = A \exp \left[\frac{-(\Delta G^{\circ} + \lambda)^2}{4\lambda kT} \right]$$