14. ENERGY AND CHARGE TRANSFER

14.1. Electronic Interactions

In this section we will describe processes that result from the interaction between two or more molecular electronic states, such as the transport of electrons or electronic excitation. This problem can be formulated in terms of a familiar Hamiltonian

$$H = H_0 + V$$

in which H_0 describes the electronic states (including any coupling to nuclear motion), and V is the interaction between the electronic states. In formulating such a problem we will need to consider some basic questions: Is V strong or weak? Are the electronic states described in a diabatic or adiabatic basis? How do nuclear degrees of freedom influence the electronic couplings? For weak couplings, we can describe the transport of electrons and electronic excitation with perturbation theory drawing on Fermi's Golden Rule:

$$\overline{w} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_{\ell} |V_{k\ell}|^2 \,\delta(E_k - E_{\ell})$$
$$\overline{w} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle$$

This approach underlies common descriptions of electronic energy transport and non-adiabatic electron transfer. We will discuss this regime concentrating on the influence of vibrational motions they are coupled to. However, the electronic couplings can also be strong, in which case the resulting states become delocalized. We will discuss this limit in the context of excitons that arise in molecular aggregates.

To begin, it is useful to catalog a number of electronic interactions of interest. We can use some schematic diagrams to illustrate them, emphasizing the close relationship between the various transport processes. However, we need to be careful, since these are not meant to imply a mechanism or meaningful information on dynamics. Here are a few commonly described processes involving transfer from a donor molecule D to an acceptor molecule A:

a) Resonance energy transfer

Applies to the transfer of energy from the electronic excited state of a donor to an acceptor molecule. Arises from a Coulomb interaction that is operative at long range, i.e., distances large compared to molecular dimensions. Requires electronic resonance. Named for the first practical derivations of expressions describing this effect: Förster Resonance Energy Transfer (FRET)



b) Electron transfer

Marcus theory. Nonadiabatic electron transfer. Requires wavefunction overlap. Ground state: $\downarrow_{(G)} \underbrace{\downarrow\uparrow} \qquad \longrightarrow \qquad \underbrace{\downarrow} \qquad \uparrow$

Excited state:

Hole transfer:

DA		D^+	A* -
<i>E</i> ⟩			↓
$ G\rangle \frac{\uparrow}{D^*} \frac{\downarrow\uparrow}{A}$	→	 D⁺	<u>↓↑</u> A*-
<i>E</i> ⟩		<u>↓</u>	
$ G\rangle \uparrow \uparrow \uparrow$		<u>↓↑</u> □*⁻	<u>^</u>

c) Electron-exchange energy transfer

Dexter transfer. Requires wavefunction overlap. Singlet or triplet



Singlet fission

d) Singlet fission



Triplet-triplet annihilation

14.2. Förster Resonance Energy Transfer

Förster resonance energy transfer (FRET) refers to the nonradiative transfer of an electronic excitation from a donor molecule to an acceptor molecule:

$$D^* + A \to D + A^* \tag{14.1}$$

This electronic excitation transfer, whose practical description was first given by Förster, arises from a dipole–dipole interaction between the electronic states of the donor and the acceptor, and does not involve the emission and reabsorption of a light field. Transfer occurs when the oscillations of an optically induced electronic coherence on the donor are resonant with the electronic energy gap of the acceptor. The strength of the interaction depends on the magnitude of a transition dipole interaction, which depends on the magnitude of the donor and acceptor transition matrix elements, and the alignment and separation of the dipoles. The sharp $1/r^6$ dependence on distance is often used in spectroscopic characterization of the proximity of donor and acceptor.

The electronic ground and excited states of the donor and acceptor molecules all play a role in FRET. We consider the case in which we have excited the donor electronic transition, and the acceptor is in the ground state. Absorption of light by the donor at the equilibrium energy gap is followed by rapid vibrational relaxation that dissipates the reorganization energy of the donor λ_D over the course of picoseconds. This leaves the donor in a coherence that oscillates at the energy gap in the donor excited state $\omega_{eg}^D(q_D = d_D)$. The time scale for FRET is typically nanoseconds, so this preparation step is typically much faster than the transfer phase. For resonance energy transfer we require a resonance condition, so that the oscillation of the excited

donor coherence is resonant with the ground state electronic energy gap of the acceptor $\omega_{eg}^{A}(q_{A}=0)$. Transfer of energy to the acceptor leads to vibrational relaxation and subsequent acceptor fluorescence that is spectrally shifted from the donor fluorescence. In practice, the efficiency of energy transfer is obtained by comparing the fluorescence emitted from donor and acceptor.



This description of the problem lends itself naturally to treating with a DHO Hamiltonian, However, an alternate picture is also applicable, which can be described through the EG Hamiltonian. FRET arises from the resonance that occurs when the fluctuating electronic energy gap of a donor in its excited state matches the energy gap of an acceptor in its ground state. In other words

$$\underbrace{\hbar \omega_{eg}^{D} - \lambda_{D}}_{\Omega_{D}(t)} = \underbrace{\hbar \omega_{eg}^{A} - \lambda_{A}}_{\Omega_{A}(t)}$$
(14.2)

These energy gaps are time-dependent with occasion crossings that allow transfer of energy.



Our system includes the ground and excited potentials of the donor and acceptor molecules. The four possible electronic configurations of the system are

$$|G_D G_A\rangle, |E_D G_A\rangle, |G_D E_A\rangle, |E_D E_A\rangle$$



 $|E_D E_A\rangle -$

Here the notation refers to the ground (G) or excited (E) vibronic states of either donor (D) or acceptor (A). More explicitly, the states also include the vibrational excitation:

$$|E_D G_A\rangle = |e_D n_D; g_A n_A\rangle$$

Thus the system can have no excitation, one excitation on the donor, one excitation on the acceptor, or one excitation on both donor and acceptor. For our purposes, let's only consider the two electronic configurations that are close in energy, and are likely to play a role in the resonance transfer in eq. (14.2)

$$\left|E_{_{D}}G_{_{A}}\right\rangle$$
 and $\left|G_{_{D}}E_{_{A}}\right\rangle$

Since the donor and acceptor are weakly coupled, we can write our Hamiltonian for this problem in a form that can be solved by perturbation theory ($H = H_0 + V$). Working with the DHO, approach, our material Hamiltonian has four electronic manifolds to consider:

$$H_{0} = |E_{D}\rangle H_{D}^{E} \langle E_{D}| + |G_{D}\rangle H_{D}^{G} \langle G_{D}| + |E_{A}\rangle H_{A}^{E} \langle E_{A}| + |G_{A}\rangle H_{A}^{G} \langle G_{A}|$$
(14.3)

Each of these is defined as we did previously, with an electronic energy and a dependence on a displaced nuclear coordinate. For instance

$$H_D^E = \left| e_D \right\rangle E_e^D \left\langle e_D \right| + H_e^D \tag{14.4}$$

$$H_e^D = \hbar \omega_0^D \left(\tilde{p}_D^2 + \left(\tilde{q}_D - \tilde{d}_D \right)^2 \right)$$
(14.5)

 E_e^D is the electronic energy of donor excited state.

Then, what is V? Classically it is a Coulomb interaction of the form

$$V = \sum_{i,j} \frac{q_i^D q_j^A}{\left| r_i^D - r_j^A \right|}$$
(14.6)

Here the sum is over all electrons and nuclei of the donor (i) and acceptor (j). As is, this is challenging to work with, but at large separation between molecules, we can recast this as a dipole–dipole interaction. We define a frame of reference for the donor and acceptor molecule, and assume that the



distance between molecules is large. Then the dipole moments for the molecules are

$$\overline{\mu}^{D} = \sum_{i} q_{i}^{D} \left(r_{i}^{D} - r_{0}^{D} \right)$$

$$\overline{\mu}^{A} = \sum_{j} q_{j}^{A} \left(r_{j}^{A} - r_{0}^{A} \right)$$
(14.7)

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

$$V = \frac{3(\overline{\mu}_A \cdot \hat{r})(\overline{\mu}_D \cdot \hat{r}) - \overline{\mu}_A \cdot \overline{\mu}_D}{\overline{r}^3}$$
(14.8)

where r is the distance between donor and acceptor dipoles and \hat{r} is a unit vector that marks the direction between them. The dipole operators here are taken to only act on the electronic states and be independent of nuclear configuration, i.e., the Condon approximation. We write the transition dipole matrix elements that couple the ground and excited electronic states for the donor and acceptor as

$$\overline{\mu}_{A} = |A\rangle \overline{\mu}_{AA^{*}} \langle A^{*} | + |A^{*}\rangle \overline{\mu}_{A^{*}A} \langle A |$$
(14.9)

$$\overline{\mu}_{D} = \left| D \right\rangle \overline{\mu}_{DD^{*}} \left\langle D^{*} \right| + \left| D^{*} \right\rangle \overline{\mu}_{D^{*}D} \left\langle D \right|$$
(14.10)

For the dipole operator, we can separate the scalar and orientational contributions as

$$\overline{\mu}_A = \hat{u}_A \,\mu_A \tag{14.11}$$

This allows the transition dipole interaction in eq. (14.8) to be written as

$$V = \mu_A \mu_B \frac{\kappa}{r^3} \left[\left| D^* A \right\rangle \left\langle A^* D \right| + \left| A^* D \right\rangle \left\langle D^* A \right| \right]$$
(14.12)

All of the orientational factors are now in the term κ .

$$\kappa = 3(\hat{u}_A \cdot \hat{r})(\hat{u}_D \cdot \hat{r}) - \hat{u}_A \cdot \hat{u}_D$$
(14.13)

We can now obtain the rates of energy transfer using Fermi's Golden Rule expressed as a correlation function in the interaction Hamiltonian:

$$w_{k\ell} = \frac{2\pi}{\hbar^2} \sum_{\ell} p_{\ell} \left| V_{k\ell} \right|^2 \delta\left(\omega_k - \omega_\ell \right) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle$$
(14.14)

Note that this is not a Fourier transform! Since we are using a correlation function there is an assumption that we have an equilibrium system, even though we are initially in the excited donor state. This is reasonable for the case that there is a clear time scale separation between the ps vibrational relaxation and thermalization in the donor excited state and the time scale (or inverse rate) of the energy transfer process.

Now substituting the initial state $\ell = |D^*A\rangle$ and the final state $k = |A^*D\rangle$, we find

$$w_{ET} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \, \frac{\left\langle \kappa^2 \right\rangle}{r^6} \left\langle D^* A \right| \mu_D(t) \, \mu_A(t) \, \mu_D(0) \, \mu_A(0) \Big| D^* A \right\rangle \tag{14.15}$$

where $\mu_D(t) = e^{iH_D t/\hbar} \mu_D e^{-iH_D t/\hbar}$. Here, we have neglected the rotational motion of the dipoles. Most generally, the orientational average is

$$\langle \kappa^2 \rangle = \langle \kappa(t) \kappa(0) \rangle$$
 (14.16)

However, this factor is easier to evaluate if the dipoles are static, or if they rapidly rotate to become isotropically distributed. For the static case $\langle \kappa^2 \rangle = 0.475$. For the case of fast loss of orientation: $\langle \kappa^2 \rangle \rightarrow \langle K(t) \rangle \langle K(0) \rangle = \langle \kappa \rangle^2 = 2/3$.

Since the dipole operators act only on $|A\rangle$ or $|D^*\rangle$, and the *D* and *A* nuclear coordinates are orthogonal, we can separate terms in the donor and acceptor states.

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

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \frac{\langle \kappa^2 \rangle}{r^6} C_{D^*D^*}(t) C_{AA}(t)$$
(14.17)

The terms in this equation represent the dipole correlation function for the donor initiating in the excited state and the acceptor correlation function initiating in the ground state. That is, these are correlation functions for the donor emission (fluorescence) and acceptor absorption. Remembering that $|D^*\rangle$ represents the electronic and nuclear configuration $|d^*n_{D^*}\rangle$, we can use the displaced harmonic oscillator Hamiltonian or energy gap Hamiltonian to evaluate the correlation functions. For the case of Gaussian statistics we can write

$$C_{D^*D^*}(t) = \left|\mu_{DD^*}\right|^2 e^{-i\left(\omega_{DD^*} - 2\lambda_D\right)t - g_D^*(t)}$$
(14.18)

$$C_{AA}(t) = \left|\mu_{AA^*}\right|^2 e^{-i\omega_{AA^*}t - g_A(t)}$$
(14.19)

Here we made use of

$$\omega_{D^*D} = \omega_{DD^*} - 2\lambda_D \tag{14.20}$$

which expresses the emission frequency as a frequency shift of $2\lambda_D$ relative to the donor absorption frequency.

The dipole correlation functions can be expressed in terms of the inverse Fourier transforms of a fluorescence or absorption lineshape:

$$C_{D^*D^*}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \ e^{-i\omega t} \ \sigma_{fluor}^D(\omega)$$
(14.21)

$$C_{AA}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \ e^{-i\omega t} \ \sigma^{A}_{abs}(\omega)$$
(14.22)

To express the rate of energy transfer in terms of its common practical form, we make use of Parsival's Theorem, which states that if a Fourier transform pair is defined for two functions, the integral over a product of those functions is equal whether evaluated in the time or frequency domain:

$$\int_{-\infty}^{\infty} f_1(t) f_2^*(t) dt = \int_{-\infty}^{\infty} \tilde{f}_1(\omega) \tilde{f}_2^*(\omega) d\omega$$
(14.23)

This allows us to express the energy transfer rate as an overlap integral J_{DA} between the donor fluorescence and acceptor absorption spectra:

$$w_{ET} = \frac{1}{\hbar^2} \frac{\langle \kappa^2 \rangle}{r^6} \left| \mu_{DD^*} \right|^2 \left| \mu_{AA^*} \right|^2 \int_{-\infty}^{+\infty} d\omega \ \mathfrak{g}^A_{abs} \left(\omega \right) \mathfrak{g}^D_{fluor} \left(\omega \right)$$
(14.24)

Here σ is the lineshape normalized to the transition matrix element squared: $\sigma = \sigma / |\mu|^2$. The overlap integral is a measure of resonance between donor and acceptor transitions.

So, the energy transfer rate scales as r^{-6} , depends on the strengths of the electronic transitions for donor and acceptor molecules, and requires resonance between donor fluorescence and acceptor absorption. One of the things we have neglected is that the rate of energy transfer will also depend on the rate of excited donor state population relaxation. Since this relaxation is



typically dominated by the donor fluorescence rate, the rate of energy transfer is commonly written in terms of an effective distance R_0 , and the fluorescence lifetime of the donor τ_D :

$$w_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{r}\right)^6 \tag{14.25}$$

At the critical transfer distance R_0 the rate (or probability) of energy transfer is equal to the rate of fluorescence. R_0 is defined in terms of the sixth-root of the terms in eq. (14.24), and is commonly written as

$$R_0^6 = \frac{9000\ln(10)\phi_D\left\langle\kappa^2\right\rangle}{128\pi^5 n^4 N_A} \int_0^\infty d\overline{\nu} \,\frac{\sigma_{\text{fluor}}^D\left(\overline{\nu}\right)\varepsilon_A\left(\overline{\nu}\right)}{\overline{\nu}^4} \tag{14.26}$$

This is the practical definition that accounts for the frequency dependence of the transitiondipole interaction and non-radiative donor relaxation in addition to being expressed in common units. $\bar{\nu}$ represents units of frequency in cm⁻¹. The fluorescence spectrum g_{fluor}^D must be normalized to unit area, so that $g_{fluor}^D(\bar{\nu})$ is expressed in cm (inverse wavenumbers). The absorption spectrum $\varepsilon_A(\bar{\nu})$ must be expressed in molar decadic extinction coefficient units (liter/mol·cm). *n* is the index of refraction of the solvent, N_A is Avagadro's number, and ϕ_D is the donor fluorescence quantum yield.

Appendix: Transition Dipole Interaction

FRET is one example of a quantum mechanical transition dipole interaction. The interaction between two dipoles, A and D, in eq. (14.12) is

$$V = \frac{\kappa}{r^3} \langle e | \mu_A | g \rangle \langle g | \mu_D | e \rangle$$
(14.27)

Here, $\langle g | \mu_D | e \rangle$ is the transition dipole moment in Debye for the ground-to-excited state transition of molecule *A*. *r* is the distance between the centers of the point dipoles, and κ is the unitless orientational factor

$$\kappa = 3\cos\theta_1\cos\theta_2 - \cos\theta_{12}$$

The figure below illustrates this function for the case of two parallel dipoles, as a function of the angle between the dipole and the vector defining their separation.



In the case of vibrational coupling, the dipole operator is expanded in the vibrational normal coordinate: $\mu = \mu_0 + (\partial \mu / \partial Q_A) Q_A$, and harmonic transition dipole matrix elements are

$$\langle 1|\mu_A|0\rangle = \sqrt{\frac{\hbar}{2c\omega_A}}\frac{\partial\mu}{\partial Q_A}$$
 (14.28)

where ω_A is the vibrational frequency. If the frequency v_A is given in cm⁻¹, and the transition dipole moment $\partial \mu / \partial Q_A$ is given in units of D Å⁻¹ amu^{-1/2}, then the matrix element in units of D is $|\langle 1 | \mu_A | 0 \rangle| = 4.1058 v_A^{-1/2} (\partial \mu / \partial Q_A)$. If the distance between dipoles is specified in Ångstroms, then the transition dipole coupling from (14.27) in cm⁻¹ is $V(cm^{-1}) = 5034\kappa r^{-3}$. Experimentally, one can determine the transition dipole moment from the absorbance *A* as

$$A = \left(\frac{\pi N_A}{3c^2}\right) \left(\frac{\partial \mu}{\partial Q_A}\right)^2$$
(14.29)

Readings

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14.3. Excitons in Molecular Aggregates

The absorption spectra of periodic arrays of interacting molecular chromophores show unique spectral features that depend on the size of the system and disorder of the environment. We will investigate some of these features, focusing on the delocalized eigenstates of these coupled chromophores, known as excitons. These principles apply to the study of molecular crystals, J-aggregates, photosensitizers, and light-harvesting complexes in photosynthesis. Similar topics are used in the description of properties of conjugated polymers and organic photovoltaics, and for extended vibrational states in IR and Raman spectroscopy.

Energy transfer in the strong coupling limit

Strong coupling between molecules leads to the delocalization of electronic or vibrational eigenstates, under which weak coupling models like FRET do not apply. From our studies of the coupled two-state system, we know that when the coupling between states is much larger that the energy splitting between the states (ε_1 - $\varepsilon_2 \ll 2V$) then the resulting eigenstates $|\pm\rangle$ are equally weighted symmetric and antisymmetric combinations of the two, whose energy eigenvalues are split by 2*V*. Setting $\varepsilon_1 = \varepsilon_2 = \varepsilon$

$$\begin{split} E_{\pm} &= \varepsilon \pm V \\ \left| \pm \right\rangle = \frac{1}{\sqrt{2}} \left(\left| 1 \right\rangle \pm \left| 2 \right\rangle \right) \end{split}$$

If we excite one of these molecules, we expect that the excitation will flow back and forth at the Rabi frequency. So, what happens with multiple coupled chromophores, focusing particular interest on the placement of coupled chromophores into periodic arrays in space? In the strong coupling regime, the variation in the uncoupled energies is small, making this a problem of coupled quasi-degenerate states. With a spatially period structure, the resulting states bear close similarity to simple descriptions of electronic band structure using the tight-binding model.

Excitons

Excitons refer to electronic excited states that are not localized to a particular molecule. But beyond that there are many flavors. We will concentrate on **Frenkel excitons**, which refer to excited states in which the excited electron and the corresponding hole (or electron vacancy) reside on the same molecule. All molecules remain electrically neutral in the ground and excited states. This corresponds to what one would expect when one has resonant dipole–dipole interactions between molecules. When there is charge transfer character, the electron and hole can reside on different molecules of the coupled complex. These are referred to as Mott–Wannier excitons.

14-12

Absorption spectrum of molecular dimer

To describe the spectroscopy of an array of many coupled chromophores, it is first instructive to work through a pair of coupled molecules. This is in essence the two-level problem from earlier. We consider a pair of molecules (1 and 2), which each have a ground and electronically excited state (|e) and |g)) split by an energy gap ε_0 , and a transition dipole moment $\overline{\mu}$. In the absence of coupling, the state of the system can be specified by specifying the electronic state of both molecules, leading to four possible states: $|gg\rangle$, $|eg\rangle$, $|ge\rangle$, $|ee\rangle$, whose energies are 0, ε_0 , ε_0 , and $2\varepsilon_0$, respectively.



For shorthand we define the ground state as $|G\rangle$ and the excited states as $|I\rangle$ and $|2\rangle$ to signify the the electronic excitation is on either molecule 1 or 2. In addition, the molecules are spaced by a separation r_{12} , and there is a transition dipole interaction that couples the molecules.

$$V = J\left(\left|2\right\rangle\left\langle1\right| + \left|1\right\rangle\left\langle2\right|\right)$$

Following our description of transition dipole coupling in Eqn. (14.8), the coupling strength J is given by

$$J = \frac{\left(\overline{\mu}_{1} \cdot \overline{\mu}_{2}\right)\left|\overline{r}_{12}\right|^{2} - 3\left(\overline{\mu}_{1} \cdot \overline{r}_{12}\right)\left(\overline{\mu}_{2} \cdot \overline{r}_{12}\right)}{\left|\overline{r}_{12}\right|^{5}} = \frac{\mu_{1}\mu_{2}}{r_{12}^{3}} \kappa$$

where the orientational factor is

$$\boldsymbol{\kappa} = (\hat{\mu}_1 \cdot \hat{\mu}_2) - 3(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12})$$

We assume that the coupling is not too strong, so that we can just concentrate on how it influences $|1\rangle$ and $|2\rangle$ but not $|G\rangle$. Then we only need to describe the coupling induced shifts to the singly excited states, which are described by the Hamiltonian



and that the eigenstates are:

$$|\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle)$$

These symmetric and antisymmetric states are delocalized across the two molecules, and in the language of Frenkel excitons are referred to as the one-exciton states. Furthermore, the dipole operator for the dimer is M_{\perp}

$$\overline{M} = \overline{\mu}_1 + \overline{\mu}_2$$

and so the transition dipole matrix elements are:

$$M_{\pm} = \left\langle \pm \left| \overline{M} \right| G \right\rangle = \frac{1}{\sqrt{2}} \left(\overline{\mu}_{1} \pm \overline{\mu}_{2} \right)$$



 M_+ and M_- are oriented perpendicular to each other in the molecular frame. If we confine the molecular dipoles to be within a plane, with an angle 2 θ between them, then the amplitude of M_+ and M_- is given by

$$M_{+} = 2\mu\cos\theta$$
$$M_{-} = 2\mu\sin\theta$$

We can now predict the absorption spectrum for the dimer. We have two transitions from the ground state and the $|\pm\rangle$ states which are resonant at $\hbar\omega = \varepsilon_0 \pm J$ and which have an amplitude $|M_{\pm}|^2$. The splitting between the peaks is referred to as the Davydov splitting. Note that the relative amplitude of the peaks allows one to infer the angle between the molecular transition dipoles. Also, note for $\theta = 0^\circ$ or 90°, all amplitude appears in one transition with magnitude $2|\mu|^2$, which is referred to as superradiant.



Now let's consider linear aggregate of N periodically arranged molecules. We will assume that each molecule is a two-level electronic system with a ground state and an excited state. We will assume that electronic excitation moves an electron from the ground state to an unoccupied orbital of the same molecule. We will label the molecules with integer values (n) between 0 and N-1:

Frenkel Excitons with Periodic Boundary Conditions



If the molecules are separated along the chain by a lattice spacing α , then the size of the chain is $L=\alpha N$. Each molecule has a transition dipole moment μ , which makes an angle β with the axis of the chain.

In the absence of interactions, we can specify the state of the system exactly by identifying whether each molecule is in the electronically excited or ground state. If the state of molecule *n* within the chain is φ_n , which can take on values of *g* or *e*, then

$$|\psi\rangle = |\varphi_0, \varphi_1, \varphi_2 \cdots \varphi_n \cdots \varphi_{N-1}\rangle$$

This representation of the state of the system is referred to as the *site basis*, since it is expressed in terms of each molecular site in the chain. For simplicity we write the ground state of the system as

$$|G\rangle = |g,g,g\ldots,g\rangle$$

If we excite one of the molecules within the aggregate, we have a singly excited state in which the n^{th} molecule is excited, so that

$$|\psi\rangle = |g, g, g, \dots, e, \dots, g\rangle \equiv |n\rangle$$

For shorthand, we identify this product state as $|n\rangle$, which is to be distinguished from the molecular eigenfunction at site n, φ_n .

The singly excited state is assigned an energy ε_0 corresponding to the electronic energy gap. In the absence of coupling, the singly excited states are *N*-fold degenerate, corresponding to a single excitation at any of the *N* sites. If two excitations are placed on the chain we can see that there are N(N-I) possible states with energy $2\varepsilon_0$, recognizing that the Pauli principle does not allow two excitations on



the same site. When coupling is introduced, the mixing of these degenerate states leads to the one-exciton and two-exciton bands. For this discussion, we will concentrate on the one-exciton states.

The coupling between molecule n and molecule n' is given by the matrix element $V_{nn'}$. We will assume that a molecule interacts only with its neighbors, and that each pairwise interaction has a magnitude J

$$V_{nn'} = J \,\delta_{n.n'\pm 1}$$

If V is a dipole–dipole interaction, the orientational factor κ dictates that when the transition dipole angle $\beta < 54.7^{\circ}$ then the sign of the coupling J < 0, which is the case known as J-aggregates (after Edwin Jelley), and implies an offset stack of chromophores or head-to-tail arrangement. If $\beta > 54.7^{\circ}$ then J > 0, and the system is known as an H-aggregate.

To begin, we also apply periodic boundary conditions to this problem, which implies that we are describing the states of an *N*-molecule chain within an infinite linear chain. In terms of the Hamiltonian, the molecules at the beginning and end of our chain feel the same symmetric interactions to two neighbors as the other molecules. To write this in terms of a finite $N \times N$ matrix, one couples the first and last member of the chain: $J_{0,N-1} = J_{N-1,0} = J$.

With these observations in mind, we can write the Frenkel Exciton Hamiltonian for the linear aggregate in terms of a system Hamiltonian that reflects the individual sites and their couplings

$$H_{0} = H_{s} + V$$

$$H_{s} = \sum_{n=1}^{N} \varepsilon_{0} |n\rangle \langle n| \qquad (14.30)$$

$$V = \sum_{n=1}^{N} J\{|n'\rangle \langle n| + |n\rangle \langle n'|\} \delta_{n,n'\pm 1}$$

Here periodic boundary conditions imply that we replace $|N\rangle \Rightarrow |0\rangle$ and $|-1\rangle \Rightarrow |N-1\rangle$ where they appear.

The optical properties of the aggregate will be obtained by determining the eigenstates of the Hamiltonian. We look for solutions that describe one-exciton eigenstates as an expansion in the site basis.

$$|\psi(x)\rangle = \sum_{n=0}^{N-1} c_n(x) |\varphi_n(x-x_n)\rangle$$
 (14.31)

which is written in order to point out the dependence of these wavefunctions on the lattice spacing x, and the position of a particular molecule at x_n . Such an expansion should work well when the electronic interactions between sites is weak enough to treat perturbatively. For the

electronic structure of solids, this is known as the tight binding model, which describes band structure as a linear combinations of atomic orbitals.

Rather than diagonalizing the Hamiltonian, we can take advantage of its translational symmetry to obtain the eigenstates. The symmetry of the Hamiltonian is such that it is unchanged by any integral number of translations along the chain. That is the results are unchanged for any summation in eqs. (14.30) and (14.31) over N consecutive integers. Similarly, the molecular wavefunction at any site is unchanged by such a translation. Written in terms of a displacement operator $D = e^{ip_x \alpha/\hbar}$ that shifts the molecular wavefunction by one lattice constant α ,

$$\left|\varphi\left(x+n\alpha\right)\right\rangle = D^{n}\left|\varphi\left(x\right)\right\rangle \tag{14.32}$$

These observations underlie Bloch's theorem, which states that the eigenstates of a periodic system will vary only by a phase shift when displaced by a lattice constant.

$$\left|\psi(x+\alpha)\right\rangle = e^{ik\alpha}\left|\psi(x)\right\rangle \tag{14.33}$$

Here k is the wavevector, or reciprocal lattice vector, a real quantity. Thus the expansion coefficients in eq. (14.31) will have an amplitude that reflects an excitation spread equally among the N sites, and only vary between sites by a spatially varying phase factor. Equivalently, the eigenstates are expected to have a form that is a product of a spatially varying phase factor and a periodic function:

$$|\psi(x)\rangle = e^{ikx}u(x) \tag{14.34}$$

These phase factors are closely related to the lattice displacement operators. If the linear chain has *N* molecules, the eigenstates must remain unchanged with a translation by the length of the chain $L = \alpha N$:

$$\left|\psi(x_n+L)\right\rangle = \left|\psi(x_n)\right\rangle$$

Therefore, we see that our wavefunctions must satisfy $e^{ikL} = 1$, or

$$Nk\alpha = 2\pi m \tag{14.35}$$

where *m* is an integer. Furthermore, since there are *N* sites on the chain, unique solutions to eq. (14.35) require that *m* can only take on *N* consecutive integer values. Like the site index *n*, there is no unique choice of *m*. Rewriting eq. (14.35), the wavevector is

$$k_m = \frac{2\pi}{\alpha} \frac{m}{N} \tag{14.36}$$

We see that for an *N* site lattice, *m* can take on the *N* consecutive integer values, so that $k_m \alpha$ varies over a 2π range of angles. The wavevector index *m* labels the *N* one-exciton eigenstates of an *N* molecule chain. By convention, k_m is chosen such that $-\pi/\alpha < k_m \le \pi/\alpha$. Then the corresponding values of *m* are integers from -(N-1)/2 to (N-1)/2 if there are an odd number of lattice sites or -(N-2)/2 to N/2 for an even number of sites. For example, a 20 molecule chain would have $m = -9, -8, \dots 9, 10$.

These findings lead to the general form for the m one-exciton eigenstates

$$\left|k_{m}\right\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ink_{m}\alpha} \left|n\right\rangle \tag{14.37}$$

The factor of $N^{1/2}$ assures proper normalization of the wavefunction, $\langle \psi | \psi \rangle = 1$. Comparing eqs. (14.37) and (14.31) we see that the expansion coefficients for the *n*th site of the *m*th eigenstate is

$$c_{m,n} = \frac{1}{\sqrt{N}} e^{i n k_m \alpha} = \frac{1}{\sqrt{N}} e^{i 2 \pi n m/N}$$
(14.38)

We see that for state $|k_0\rangle$, with m = 0, the phase factor is the same for all sites. In other words, the transition dipoles of the chain will oscillate in-phase, constructively adding for all sites. For the case that $k_m = \pi/\alpha$, we see that each site is out-of-phase with its nearest neighbors. Looking at the case of the dimer, N = 2, we see that m = 0 or 1, $k_m = 0$ or π/α , and we recover the expected symmetric and antisymmetric eigenstates:

$$|k_{0}\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^{1} e^{in \cdot 0} |n\rangle = \frac{1}{\sqrt{2}} (|0\rangle + |1\rangle) \qquad (k=0)$$
$$|k_{1}\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^{1} e^{in\pi} |n\rangle = \frac{1}{\sqrt{2}} (|0\rangle - |1\rangle) \qquad (k = \pi / \alpha)$$

Schematically for N = 20, we see how the dipole phase varies with k_m , plotting the real and imaginary components of the expansion coefficients



Also, we can evaluate the one-exciton transition dipole matrix elements, $M(k_m)$, which are expressed as superpositions of the dipole moments at each site, $\overline{\mu}_n$:

$$\overline{M} = \sum_{n=0}^{N-1} \overline{\mu}_n \tag{14.39}$$

$$M_{m} = \langle k_{m} | \overline{M} | G \rangle$$

= $\frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ink_{m}\alpha} \langle n | \overline{\mu}_{n} | G \rangle$ (14.40)

The phase of the transition dipoles of the chain matches their phase within each *k* state. Thus for our problem, in which all of the dipoles are parallel, transitions from the ground state to the $k_m=0$ state will carry all of the oscillator strength. Plotted below is an illustration of the phase relationships between dipoles in a chain with N = 20.



Finally, let's solve for the one-exciton energy eigenvalues by calculating the expectation value of the Hamiltonian operator, eq. (14.30)

$$E(k_{m}) = \langle k | H_{0} | k \rangle$$

$$= \frac{1}{N} \sum_{n,m=0}^{N-1} e^{i(n-m)k\alpha} \langle m | H_{0} | n \rangle$$

$$\langle k_{m} | H_{S} | k_{m} \rangle = \frac{1}{N} \sum_{n=0}^{N-1} \varepsilon_{0} = \varepsilon_{0}$$

$$\langle k_{m} | V | k_{m} \rangle = \frac{1}{N} \sum_{n=0}^{N-1} \left\{ e^{ik_{m}\alpha} \langle n-1 | V | n \rangle + e^{-ik_{m}\alpha} \langle n+1 | V | n \rangle \right\}$$

$$= 2J \cos(k_{m}\alpha)$$

$$E(k_{m}) = \varepsilon_{0} + 2J \cos(k_{m}\alpha) \qquad (14.42)$$

You predict that the one-exciton band of states varies in energy between $\varepsilon_0 - 2J$ and $\varepsilon_0 + 2J$. If we take J as negative, as expected for the case of J-aggregates (negative couplings), then k = 0 is at the bottom of the band. Examples are illustrated below for the N=20 aggregate.



Note that the result in eq. (14.42) gives you a splitting of 4J between the two states of the dimer, unlike the expected 2J splitting from earlier. This is a result of the periodic boundary conditions that we enforce here.

We are now in a position to plot the absorption spectrum for aggregate, summing over eigenstates and assuming a Lorentzian lineshape for the system:

$$\sigma(\omega) = \sum_{m} |M_{m}|^{2} \frac{\Gamma^{2}}{(\hbar \omega - E(k_{m})) + \Gamma^{2}}$$

For a 20 oscillator chain with negative coupling, the spectrum is plotted below. We have one peak corresponding to the k_0 mode that is peaked at $\hbar \omega = \varepsilon_0 - 2J$ and carries the oscillator strength of all 20 dipoles.



Open Boundary Conditions

Similar types of solutions appear without using periodic boundary conditions. For the case of open boundary conditions, in the molecules at the end of the chain are only coupled to the one nearest neighbor in the chain. In this case, it is helpful to label on the sites from n = 1, 2...N. Furthermore, m = 1, 2...N. Under those conditions, one can solve for the eigenstates using use the boundary condition that $\psi = 0$ at sites 0 and N+1. The change in boundary condition gives *sine* solutions:

$$\left|k_{m}\right\rangle = \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin\left(\frac{\pi mn}{N+1}\right) \left|n\right\rangle$$

The energy eigenvalues are

$$E_m = \omega_0 + 2J \cos\left(\frac{\pi m}{N+1}\right)$$

Returning to the case of the dimer (N=2), we can now confirm that we recover the symmetric and anti-symmetric eigenstates, with an energy splitting of 2J.

If you calculate the oscillator strength for these transitions using the dipole operator in eq. (14.39), one finds:

$$M_{m}^{2} = \left| \left\langle k_{m} \left| \overline{M} \right| G \right\rangle \right|^{2} = \left(\frac{1 - (-1)^{m}}{2} \right)^{2} \frac{2\mu^{2}}{N + 1} \cot^{2} \left(\frac{\pi m}{2(N + 1)} \right)$$

This result shows that most of the oscillator strength lies in the m=1 state, for which all oscillators are in phase. For large N, M_1^2 carries 81% of the oscillator strength, with approximately 9% in the transition to the m=3 state.



The shift in the peak of the absorption relative to the monomer gives the coupling J. Including long-range interactions has the effect of shifting the exciton band asymmetrically about ω_0 .

 $\Omega_1 = \omega_0 + 2.4J$ (*m*=1, bottom of the band with *J* negative) $\Omega_N = \omega_0 - 1.8J$ (Top of band)

Exchange Narrowing

If the chain is <u>not</u> homogeneous, i.e., all molecules do not have same site energy ε_0 , then we can model this effect as Gaussian random disorder. The energy of a given site is

$$\varepsilon_n = \varepsilon_0 + \delta \omega_n$$

We add as an extra term to our earlier Hamiltonian, eq. (14.30), to account for this variation.

$$H_{0} = H_{S} + H_{dis} + V$$
$$H_{dis} = \sum_{n} \delta \omega_{n} |n\rangle \langle n|$$

The effect is to shift and mix the homogeneous exciton states.

$$\delta\Omega_{k} = \left\langle k \left| H_{dis} \right| k \right\rangle = \frac{2}{N+1} \sum_{n} \sin^{2} \left(\frac{\pi kn}{N+1} \right) \delta\omega_{n}$$

We find that these shifts are also Gaussian random variables, with a standard deviation of $\Delta\sqrt{3/2(N+1)}$, where Δ is the standard deviation for site energies. So, the delocalization of the eigenstate averages the disorder over N sites, which reduces the distribution of energies by a factor scaling as \sqrt{N} . The narrowing of the absorption lineshape with delocalization is called exchange narrowing. This depends on the distribution of site energies being relatively small: $\Delta << 3\pi |J| / N^{3/2}$.



Readings

 Knoester, J., Optical Properties of Molecular Aggregates. In *Proceedings of the International* School of Physics "Enrico Fermi" Course CXLIX, Agranovich, M.; La Rocca, G. C., Eds. IOS Press: Amsterdam, 2002; pp 149-186.

14.4. Multiple Particles and Second Quantization

In the case of a large number of nuclear or electronic degrees of freedom (or for photons in a quantum light field), it becomes tedious to write out the explicit product-state form of the state vector, i.e.,

$$|\psi\rangle = |\varphi_1, \varphi_2, \varphi_3 \dots\rangle$$

Under these circumstances it becomes useful to define creation and annihilation operators. If $|\psi\rangle$ refers to the state of multiple harmonic oscillators, then the Hamiltonian has the form

$$H = \sum_{\alpha} \left(\frac{p_{\alpha}^{2}}{2m_{\alpha}} + \frac{1}{2}m_{\alpha}\omega_{\alpha}^{2}q_{\alpha}^{2} \right)$$
(14.43)

which can also be expressed as

$$H = \sum_{\alpha} \hbar \omega_{\alpha} \left(a_{\alpha}^{\dagger} a_{\alpha} + \frac{1}{2} \right)$$
(14.44)

and the eigenstates represented in through the occupation of each oscillator $|\psi\rangle = |n_1, n_2, n_3...\rangle$. This representation is sometimes referred to as "second quantization", because the classical Hamiltonian was initially quantized by replacing the position and momentum variables by operators, and then these quantum operators were again replaced by raising and lowering operators.

The operator a_{α}^{\dagger} raises the occupation in mode $|n_{\alpha}\rangle$, and a_{α} lowers the excitation in mode $|n_{\alpha}\rangle$. The eigenvalues of these operators, $n_{\alpha} \rightarrow n_{\alpha} \pm 1$, are captured by the commutator relationships:

$$\left[a_{\alpha}, a_{\beta}^{\dagger}\right] = \delta_{\alpha\beta} \tag{14.45}$$

$$\left[a_{\alpha}, a_{\beta}\right] = 0 \tag{14.46}$$

Eqn. (14.45) indicates that the raising and lower operators do not commute if they are operators in the same degree of freedom ($\alpha=\beta$), but they do otherwise. Written another way, these expression indicate that the order of operations for the raising and lowering operators in different degrees of freedom commute.

$$a_{\alpha}a_{\beta}^{\dagger} = a_{\beta}^{\dagger}a_{\alpha} \tag{14.47}$$

$$a_{\alpha}a_{\beta} = a_{\beta}a_{\alpha} \tag{14.48}$$

$$a^{\dagger}_{lpha}a^{\dagger}_{eta}=a^{\dagger}_{eta}a^{\dagger}_{lpha}$$

These expressions also imply that the eigenfunctions operations of the forms in eq. (14.47) and (14.48) are the same, so that these eigenfunctions should be symmetric to interchange of the coordinates. That is, these particles are bosons.

This observations proves an avenue to defining raising and lowering operators for electrons. Electrons are fermions, and therefore antisymmetric to exchange of particles. This suggests that electrons will have raising and lowering operators that change the excitation of an electronic state up or down following the relationship

$$b_{\alpha}b_{\beta}^{\dagger} = -b_{\beta}^{\dagger}b_{\alpha} \tag{14.49}$$

or

$$\left[b_{\alpha}, b_{\beta}^{\dagger}\right]_{+} = \delta_{\alpha\beta} \tag{14.50}$$

where [...]+ refers to the anti-commutator. Further, we write

$$\left[b_{\alpha}, b_{\beta}\right]_{+} = 0 \tag{14.51}$$

This comes from considering the action of these operators for the case where $\alpha = \beta$. In that case, taking the Hermetian conjugate, we see that eq. (14.51) gives

$$2b_{\alpha}^{\dagger}b_{\alpha}^{\dagger} = 0 \quad \text{or} \quad b_{\alpha}^{\dagger}b_{\alpha}^{\dagger} = 0 \tag{14.52}$$

This relationship says that we cannot put two excitations into the same state, as expected for Fermions. This relationship indicates that there are only two eigenfunctions for the operators b_{α}^{\dagger} and b_{α} , namely $|n_{\alpha} = 0\rangle$ and $|n_{\alpha} = 1\rangle$. This is also seen with eq. (14.50), which indicates that $b_{\alpha}^{\dagger}b_{\alpha}|n_{\alpha}\rangle + b_{\alpha}b_{\alpha}^{\dagger}|n_{\alpha}\rangle = |n_{\alpha}\rangle$

or

$$b_{\alpha}b_{\alpha}^{\dagger}|n_{\alpha}\rangle = (1 - b_{\alpha}^{\dagger}b_{\alpha})|n_{\alpha}\rangle$$
(14.53)

If we now set $|n_{\alpha}\rangle = |0\rangle$, we find that eq. (14.53) implies

$$b_{\alpha}b_{\alpha}^{\dagger}|0\rangle = |0\rangle$$

$$b_{\alpha}^{\dagger}b_{\alpha}|0\rangle = 0$$

$$b_{\alpha}b_{\alpha}^{\dagger}|1\rangle = 0$$

$$b_{\alpha}^{\dagger}b_{\alpha}|1\rangle = |1\rangle$$
(14.54)

Again, this reinforces that only two states, $|0\rangle$ and $|1\rangle$, are allowed for electron raising and lowering operators. These are known as Pauli operators, since they implicitly enforce the Pauli exclusion principle. Note, in eq. (14.54), that $|0\rangle$ refers to the eigenvector with an eigenvalue of zero $|\phi_0\rangle$, whereas "0" refers to the null vector.

Frenkel Excitons

For electronic chromophores, we use the notation $|g\rangle$ and $|e\rangle$ for the states of an electron in its ground or excited state. The state of the system for one excitation in an aggregate

$$|n\rangle = |g,g,g,g...e...g\rangle$$

can then be written as $a_n^{\dagger} | G \rangle$, or simply a_n^{\dagger} , and the Frenkel exciton Hamiltonian is

$$H_{0} = \sum_{n=0}^{N-1} \varepsilon_{0} |n\rangle \langle n| + \sum_{n,m} J_{n,m} |n\rangle \langle m|$$
(14.55)

or

$$=\sum_{n}\varepsilon_{0}b_{n}^{\dagger}b_{n}+\sum_{n,m}J_{n,m}b_{n}^{\dagger}b_{m}$$
(14.56)

Readings

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14.5. Marcus Theory For Electron Transfer

The displaced harmonic oscillator (DHO) formalism and the Energy Gap Hamiltonian have been used extensively in describing charge transport reactions, such as electron and proton transfer. Here we describe the rates of electron transfer between weakly coupled donor and acceptor states when the potential energy depends on a nuclear coordinate, i.e., nonadiabatic electron transfer. These results reflect the findings of Marcus' theory of electron transfer.

We can represent the problem as calculating the transfer or reaction rate for the transfer of an electron from a donor to an acceptor

$$D + A \to D^+ + A^- \tag{14.57}$$

This reaction is mediated by a nuclear coordinate q. This need not be, and generally isn't, a simple vibrational coordinate. For electron transfer in solution, we most commonly consider electron transfer to progress along a solvent rearrangement coordinate in which solvent reorganizes its configuration so that dipoles or charges help to stabilize the extra negative charge at the acceptor site. This type of *collective* coordinate is illustrated in the figure to the right. The external response of the medium along the electron transfer coordinate is referred to as "outer shell" electron transfer, whereas the influence of internal vibrational modes that promote ET is called "inner shell". The influence of collective solvent rearrangements or

intramolecular vibrations can be captured with the use of an electronic transition coupled to a harmonic bath.

Normally we associate the rates of electron transfer with the free-energy along the

electron transfer coordinate q. Pictures such as the ones above that illustrate states of the system with electron localized on the donor or acceptor electrons hopping from donor to acceptor are conceptually represented through diabatic energy surfaces. The electronic coupling J that results in transfer mixes these diabatic states in the crossing region. From this adiabatic surface, the rate of transfer for the forward reaction is related to the flux across the barrier. From

classical transition state theory we can associate the rate with the free energy barrier using $k_f = A \exp(-\Delta G^{\dagger}/k_B T)$. If the coupling is weak, we can describe the rates of transfer between





donor and acceptor in the diabatic basis with perturbation theory. This accounts for nonadiabatic effects and tunneling through the barrier.

To begin we consider a simple classical derivation for the free-energy barrier and the rate of electron transfer from donor to acceptor states for the case of weakly coupled diabatic states. First we assume that the free energy or potential of mean force for the



initial and final state, $G(q) = -k_BT \ln P(q)$, is well represented by two parabolas.

$$G_{D}(q) = \frac{1}{2} m \omega_{0}^{2} (q - d_{D})^{2}$$

$$G_{A}(q) = \frac{1}{2} m \omega_{0}^{2} (q - d_{A})^{2} + \Delta G^{0}$$
(14.58)

To find the barrier height ΔG^{\ddagger} , we first find the crossing point $d_{\rm C}$ where $G_{\rm D}(d_{\rm C}) = G_{\rm A}(d_{\rm C})$. Substituting eq. and solving for $d_{\rm C}$ gives

$$\frac{1}{2}m\omega_0^2 (d_C - d_D)^2 = \Delta G^\circ + \frac{1}{2}m\omega_0^2 (d_C - d_A)^2$$
$$d_C = \frac{\Delta G^\circ}{m\omega_0^2} \left(\frac{1}{d_A - d_D}\right) + \frac{d_A + d_D}{2}$$
$$= \frac{\Delta G^\circ}{2\lambda} (d_A - d_D) + \frac{d_A + d_D}{2}$$

The last expression comes from the definition of the reorganization energy, which is the energy to be dissipated on the acceptor surface if the electron is transferred at d_D ,

$$\lambda = G_A(d_D) - G_A(d_A)$$

= $\frac{1}{2}m\omega_0^2 (d_D - d_A)^2$ (14.59)

Then, the free energy barrier to the transfer ΔG^{\ddagger} is

$$\Delta G^{\ddagger} = G_D(d_C) - G_D(d_D)$$
$$= \frac{1}{2}m\omega_0^2(d_C - d_D)^2$$
$$= \frac{1}{4\lambda}[\Delta G^\circ + \lambda]^2$$

So the Arrhenius rate constant is for electron transfer via activated barrier crossing is

$$k_{ET} = A \exp\left[\frac{-(\Delta G^{\circ} + \lambda)^2}{4\lambda kT}\right]$$
(14.60)

This curve qualitatively reproduced observations of a maximum electron transfer rate under the conditions $-\Delta G^{\circ} = \lambda$, which occurs in the barrierless case when the acceptor parabola crosses the donor state energy minimum.

We expect that we can more accurately describe nonadiabatic electron transfer using the DHO or Energy Gap Hamiltonian, which will include the possibility of tunneling through the barrier when donor and acceptor wavefunctions overlap. We start by writing the transfer rates in



terms of the potential energy as before. We recognize that when we calculate thermally averaged transfer rates that this is equivalent to describing the diabatic free energy surfaces. The Hamiltonian is

$$H = H_0 + V \tag{14.61}$$

$$H_{0} = \left| D \right\rangle H_{D} \left\langle D \right| + \left| A \right\rangle H_{A} \left\langle A \right|$$
(14.62)

Here $|D\rangle$ and $|A\rangle$ refer to the potential where the electron is either on the donor or acceptor, respectively. Also remember that $|D\rangle$ refers to the vibronic states $|d,nd\rangle$. These are represented through the same harmonic potential, displaced from one another vertically in energy by

$$\Delta E = E_A - E_L$$

and horizontally along the reaction coordinate q:

$$H_{D} = |d\rangle E_{D} \langle d| + H_{d}$$

$$H_{A} = |a\rangle E_{A} \langle a| + H_{a}$$
(14.63)

$$H_{d} = \hbar \omega_{0} \left(\underbrace{p}^{2} + (\underbrace{q} - \underbrace{d}_{D})^{2} \right)$$

$$H_{a} = \hbar \omega_{0} \left(\underbrace{p}^{2} + (\underbrace{q} - \underbrace{d}_{A})^{2} \right)$$
(14.64)

Here we are using reduced variables for the momenta, coordinates, and displacements of the harmonic oscillator. The diabatic surfaces can be expressed as product states in the electronic and nuclear configurations: $|D\rangle = |d, n\rangle$. The interaction between the surfaces is assigned a coupling *J*

$$V = J\left[\left|d\right\rangle\left\langle a\right| + \left|a\right\rangle\left\langle d\right|\right]$$
(14.65)

(14.60)

We have made the Condon approximation, implying that the transfer matrix element that describes the electronic interaction has no dependence on nuclear coordinate. Typically this electronic coupling is expected to drop off exponentially with the separation between donor and acceptor orbitals;

$$J = J_0 \exp\left(-\beta_E \left(R - R_0\right)\right) \tag{14.66}$$

Here β_E is the parameter governing the distance dependence of the overlap integral. For our purposes, even though this is a function of donor-acceptor separation (*R*), we take this to vary slowly over the displacements investigated here, and therefore be independent of the nuclear coordinate (*Q*).

Marcus evaluated the perturbation theory expression for the transfer rate by calculating Franck-Condon factors for the overlap of donor and acceptor surfaces, in a manner similar to our treatment of the DHO electronic absorption spectrum. Similarly, we can proceed to calculate the rates of electron transfer using the Golden Rule expression for the transfer of amplitude between two states

$$w_{k\ell} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \left\langle V_I(t) V_I(0) \right\rangle$$
(14.67)

Using $V_I(t) = e^{iH_0t/\hbar} V e^{-iH_0t/\hbar}$, we write the electron transfer rate in the DHO eigenstate form as

$$w_{ET} = \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \, e^{-i\Delta E t/\hbar} F(t)$$
 (14.68)

where

$$F(t) = \langle e^{-tx} e^{-tx} \rangle \tag{14.09}$$

This form emphasizes that the electron transfer rate is governed by the overlap of vibrational wavepackets on the donor and acceptor potential energy surfaces.

 $E(t) / a^{iH_dt/\hbar} - iH_dt/\hbar$

Alternatively, we can cast this in the form of the Energy Gap Hamiltonian. This carries with is a dynamical picture of the electron transfer event. The energy of the two states have time-dependent (fluctuating) energies as a result of their interaction

with the environment. Occasionally the energy of the donor and acceptor states coincide that is the energy gap between them is zero. At this point transfer becomes efficient. By integrating over the correlation function for these energy gap fluctuations, we characterize the statistics for barrier crossing, and therefore forward electron transfer.

Similar to before, we define a donor-acceptor energy gap Hamiltonian

$$H_{AD} = H_A - H_D \tag{14.70}$$



(14.72)

which allows us to write

$$F(t) = \left\langle \exp_{+}\left[-\frac{i}{\hbar}\int_{0}^{t} dt' H_{AD}(t')\right] \right\rangle$$
(14.71)

and

These expressions and application of the cumulant expansion to eq. allows us to express the transfer rate in terms of the lineshape function and correlation function

 $H_{AD}(t) = e^{iH_d t/\hbar} H_{AD} e^{-iH_d t/\hbar}$

$$F(t) = \exp\left[\frac{-i}{\hbar} \langle H_{AD} \rangle t - g(t)\right]$$
(14.73)

$$g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 C_{AD}(\tau_2 - \tau_1)$$
(14.74)

$$C_{AD}(t) = \frac{1}{\hbar^2} \left\langle \delta H_{AD}(t) \delta H_{AD}(0) \right\rangle$$
(14.75)

$$\langle H_{AD} \rangle = \lambda$$
 (14.76)

The lineshape function can also be written as a sum of many coupled nuclear coordinates, q_{α} . This expression is commonly applied to the vibronic (inner shell) contributions to the transfer rate:

$$g(t) = -\sum_{\alpha} \left(\underline{d}_{\alpha}^{A} - \underline{d}_{\alpha}^{D} \right)^{2} \left[\left(\overline{n}_{\alpha} + 1 \right) \left(e^{-i\omega_{\alpha}t} - 1 + i\omega_{0}t \right) + \overline{n}_{\alpha} \left(e^{i\omega_{\alpha}t} - 1 - i\omega_{0}t \right) \right]$$

$$= -\sum_{\alpha} \left(\underline{d}_{\alpha}^{A} - \underline{d}_{\alpha}^{D} \right)^{2} \left[\coth\left(\beta\hbar\omega_{\alpha}/2\right) \left(\cos\omega_{\alpha}t - 1\right) - i\left(\sin\omega_{\alpha}t - \omega_{\alpha}t\right) \right]$$
(14.77)

Substituting the expression for a single harmonic mode into the Golden Rule rate expression eq. gives

$$w_{ET} = \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \, e^{-i\Delta Et/\hbar - g(t)}$$
$$= \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \, e^{-i(\Delta E + \lambda)t/\hbar} \exp\left[D\left(\coth\left(\beta\hbar\omega_0/2\right)\left(\cos\omega_0 t - 1\right) - i\sin\omega_0 t\right)\right] \quad (14.78)$$

where

$$D = \left(\underline{d}_A - \underline{d}_D\right)^2 \tag{14.79}$$

This expression is very similar to the one that we evaluated for the absorption lineshape of the Displaced Harmonic Oscillator model. A detailed evaluation of this vibronically mediated transfer rate is given in Jortner.

To get a feeling for the dependence of k on q, we can look at the classical limit $\hbar\omega \ll kT$. This corresponds to the case where one is describing the case of a low frequency

"solvent mode" or "outer sphere" effect on the electron transfer. Now, we neglect the imaginary part of g(t) and take the limit $\coth(\beta\hbar\omega/2) \rightarrow 2/\beta\hbar\omega$:

$$w_{ET} = \frac{\left|J\right|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \, e^{-i(\Delta E + \lambda)t} \, \exp\left(-\left(\frac{2Dk_B T}{\hbar\omega_0}\right) (1 - \cos\omega_0 t)\right) \tag{14.80}$$

Note that the high temperature limit also means the low frequency limit for ω_0 . This means that we can expand $\cos \omega_0 t \approx 1 - (\omega_0 t)^2 / 2$, and find

$$w_{ET} = \frac{\left|J\right|^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp\left[\frac{-\left(\Delta E + \lambda\right)^2}{4\lambda kT}\right]$$
(14.81)

where $\lambda = D\hbar\omega_0$. Note that the activation barrier ΔE^{\dagger} for displaced harmonic oscillators is $\Delta E^{\dagger} = \Delta E + \lambda$. For a thermally averaged rate it is proper to associate the average energy gap with the standard free energy of reaction, $\langle H_A - H_D \rangle - \lambda = \Delta G^0$. Therefore, this expression is equivalent to the classical Marcus' result for the electron transfer rate

$$k_{ET} = A \exp\left[\frac{-\left(\Delta G^{o} + \lambda\right)^{2}}{4\lambda kT}\right]$$
(14.82)

where the pre-exponential is

$$A = 2\pi \left| J \right|^2 / \hbar \sqrt{4\pi\lambda kT} \tag{14.83}$$

This expression shows the nonlinear behavior expected for the dependence of the electron transfer rate on the driving force for the forward transfer, i.e., the reaction free energy. This is unusual because we generally think in terms of a linear free energy relationship between the rate of a reaction and the equilibrium constant: $\ln k \propto \ln K_{eq}$. This leads to the thinking that the rate should increase as we increase the driving free energy for the reaction $-\Delta G^0$. This behavior only hold for a small region in ΔG^0 . Instead, eq. shows that the ET rate will increase with $-\Delta G^0$, until a maximum rate is observed for $-\Delta G^0 = \lambda$ and the rate then decreases. This decrease of k with increased $-\Delta G^0$ is known as the "inverted regime". The inverted



behavior means that extra vibrational excitation is needed to reach the curve crossing as the acceptor well is lowered. The high temperature behavior for coupling to a low frequency mode (100 cm⁻¹ at 300 K) is shown at right, in addition to a cartoon that indicates the shift of the curve crossing at ΔG^0 is increased.

Particularly in intramolecular ET, it is common that one wants to separately account for the influence of a high frequency intramolecular vibration (inner sphere ET) that is not in the classical limit that applies to the low frequency classical solvent response. If an additional mode of frequency ω_0 and a rate in the form eq. is added to the low frequency mode, Jortner has given an expression for the rate as:

$$w_{ET} = \frac{\left|J\right|^2}{\hbar} \sqrt{\frac{\pi}{\lambda_0 kT}} \sum_{j=0}^{\infty} \left(\frac{e^{-D}}{j!} D^j\right) \exp\left[\frac{-\left(\Delta G^o + \lambda_0 + j\hbar\omega_0\right)^2}{4\lambda_0 kT}\right]$$
(14.84)

Here λ_0 is the solvation reorganization energy. For this case, the same inverted regime exists; although the simple Gaussian dependence of k on ΔG^0 no longer exists. The asymmetry here exists because tunneling sees a narrower barrier in the inverted regime than in the normal regime. Examples of the rates obtained with eq. are plotted in the figure below (T= 300K).



As with electronic spectroscopy, a more general and effective way of accounting for the nuclear motions that mediate the electron transfer process is to describe the coupling weighted density of states as a spectral density. Then we can use coupling to a harmonic bath to describe solvent and/or vibrational contributions of arbitrary form to the transfer event using

$$g(t) = \int_0^\infty d\omega \ \rho(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) (1 - \cos\omega t) + i(\sin\omega t - \omega t) \right]$$
(14.85)

Readings

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