Title:Marcus Hush Theory

Course:M.Sc Chemistry

Semester 1

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The displaced harmonic oscillator (DHO) formalism and the Energy Gap Hamiltonian have been used extensively in describing charge transport reaction, 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., non-adiabatic 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

$$D + A \rightarrow D^+ + A^-$$ (12.22)

This reaction is mediated by a nuclear coordinate q. This need not be, and generally isn't, a simple local 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. The electronic coupling that leads to transfer mixes the diabatic states that define the potential with the electron on the donor or on the acceptor in the region of their crossing. From this adiabatic surface, we would obtain the rate of transfer from $k = \exp\left(-\Delta G^\ddagger / kT\right)$. If the coupling is weak, and the splitting is small at the crossing point, we
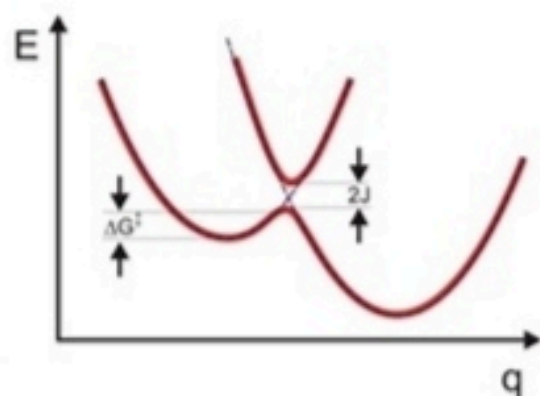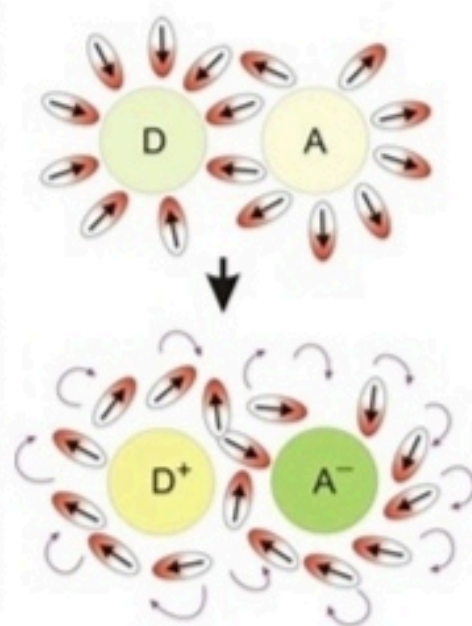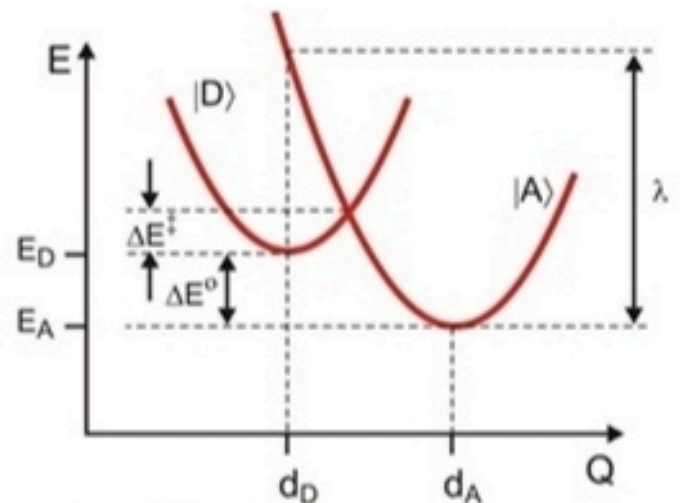
can work in the diabatic basis and use perturbation theory to calculate the rate of transfer between surfaces. This accounts for non-adiabatic effects and tunneling through the barrier.

Here we will 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 surfaces through a potential of mean force. The Hamiltonian is

$$H = H_0 + V \tag{12.23}$$

$$H_0 = |D\rangle H_D \langle D| + |A\rangle H_A \langle A| \tag{12.24}$$

Here $|D\rangle$ and $|A\rangle$ refer to the potential where the electron is either on the donor or acceptor, respectively. These are represented through the same harmonic potential, displaced from one another vertically in energy and horizontally along the reaction coordinate q:

$$H_D = E_D + \hbar\omega_0 \left(\underline{p}^2 + (q - \underline{d}_D)^2 \right)$$
$$H_A = E_A + \hbar\omega_0 \left(\underline{p}^2 + (q - \underline{d}_A)^2 \right) \tag{12.25}$$

Here we are using reduced variables for the momenta, coordinates, and displacements of the harmonic oscillator. These are Born-Oppenheimer surfaces which we can express as product states in the electronic and nuclear configurations: $|D\rangle = |d, n\rangle$. The coupling between the surfaces is assigned a coupling matrix element J

$$V = J \left[|d\rangle\langle a| + |a\rangle\langle d| \right]. \tag{12.26}$$

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.

$$J = J_0 \exp\left(-\beta(R - R_0) \right). \tag{12.27}$$

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

$$w_{k\ell} = \frac{2\pi}{\hbar} \sum_\ell p_\ell |V_{k\ell}|^2 \delta(E_k - E_\ell) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle \tag{12.28}$$

Using $V_I(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}$ we write the electron transfer rate in the DHO eigenstate form as

$$w_{ET} = \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i(E_A - E_D)t/\hbar} \left\langle e^{iH_D t/\hbar} e^{-iH_A t/\hbar} \right\rangle \tag{12.29}$$

or in the form of the Energy Gap Hamiltonian

$$w_{ET} = \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i(E_A - E_D)t/\hbar}\, F(t) \tag{12.30}$$

where

$$F(t) = \left\langle \exp_+ \left[-\frac{i}{\hbar} \int_0^t dt'\, H_{DA}(t') \right] \right\rangle, \tag{12.31}$$

$$H_{DA} = H_A - H_D, \tag{12.32}$$

and

$$H_{DA}(t) = e^{iH_D t/\hbar} H_{DA}\, e^{-iH_D t/\hbar}. \tag{12.33}$$

These expressions and application of the cumulant expansion to eq. (12.31) allows us to express the transfer rate in terms of the lineshape function and correlation function

$$F(t) = \exp\left[\frac{-i}{\hbar} \lambda t - g(t) \right] \tag{12.34}$$

$$g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1\, C_{DA}(\tau_2 - \tau_1) \tag{12.35}$$

$$C_{DA}(t) = \frac{1}{\hbar^2} \langle \delta H_{DA}(t) \delta H_{DA}(0) \rangle \tag{12.36}$$

$$\lambda = \langle H_{DA} \rangle \tag{12.37}$$

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:

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

$$= \sum_\alpha \left(\underset{\sim}{d}_\alpha^A - \underset{\sim}{d}_\alpha^D \right)^2 \left[\coth\left(\beta \hbar \omega_\alpha / 2 \right)\left(1 - \cos \omega_\alpha t \right) + i\left(\sin \omega_\alpha t - \omega_\alpha t \right) \right] \tag{12.38}$$

Substituting the expression for a single harmonic mode into the Golden Rule rate expression eq. (12.28) gives

$$W_{ET} = \frac{|J|^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i(E_A - E_D + \lambda)t} \exp\left[D\left((\bar{n}+1)\left(e^{-i\omega_0 t} + 1 \right) + \bar{n}\left(e^{i\omega_0 t} - 1 \right) \right) \right] \tag{12.39}$$

where
$$D = \left(\underset{\sim}{d}_A - \underset{\sim}{d}_D \right)^2. \tag{12.40}$$

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.[2]

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 $\coth\left(\beta\hbar\omega/2 \right) \rightarrow 2/\beta\hbar\omega$:

$$W_{ET} = \frac{J^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i(E_A - E_D + \lambda)t} \exp\left(-(2DkT/\hbar\omega_0)\left(1 - \cos\omega_0 t \right) \right) \tag{12.41}$$

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

$$W_{ET} = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp\left[\frac{-(E_A - E_D + \lambda)^2}{4\lambda kT} \right] \tag{12.42}$$

where $\lambda = D\hbar\omega_0$. Note that the activation barrier $\Delta E^\ddagger$ for displaced harmonic oscillators is $\Delta E^\ddagger = E_A - E_D + \lambda = \Delta E^0 + \lambda$. For a thermally averaged rate it is proper to associate the average energy gap with the standard free energy of reaction, $\langle H_A - H_D \rangle - \lambda = \Delta G^0$.[3] Therefore, this expression is equivalent to Marcus' result for the electron transfer rate[4]

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

(12.43)

where the pre-exponential is

$$A = 2\pi|J|^2/\hbar\sqrt{4\pi\lambda kT}.$$

(12.44)

This expression shows the nonlinear behavior expected for the dependence of the electron transfer rate on 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. (12.43) 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.
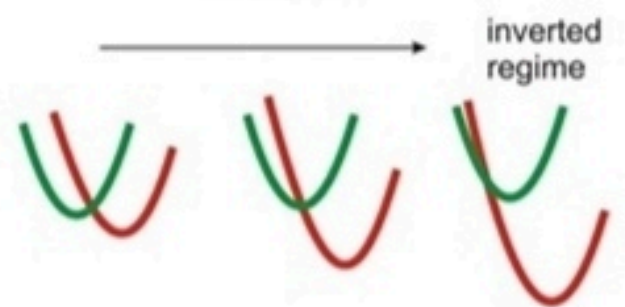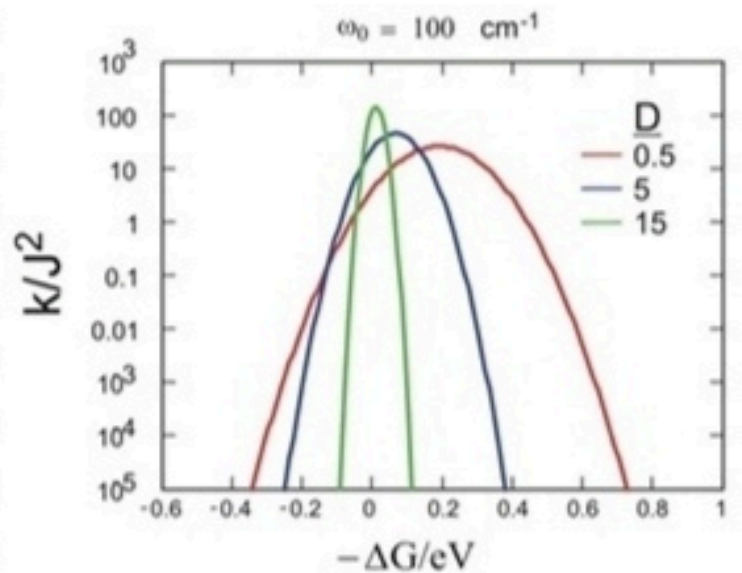
Particularly in intramolecular ET, it is common that one wants to also account for the influence of a high frequency intramolecular vibration that is not in the classical limit. If an additional mode of frequency ω_a and a rate in the form eq. (12.39) is added to the low frequency mode, Jortner has given an expression for the rate as:

$$w_{ET} = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda_0 kT}} \sum_{j=0}^{\infty} \left(\frac{e^{-D}}{j!} D^j \right) \exp\left[\frac{-\left(\Delta G^o + \lambda_0 + j\hbar\omega_0\right)^2}{4\lambda_0 kT} \right]. \tag{12.45}$$

Here λ_0 is the reorganization energy under the low frequency mode, and ω_0 is the frequency of the high frequency mode. 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. (12.45) are plotted in the figure below (T= 300K).

Vibrational frequency: $\omega_0 := 2000$ cm^{-1}
Solvent reorganization energy: $\lambda_0 := 0.5$ eV
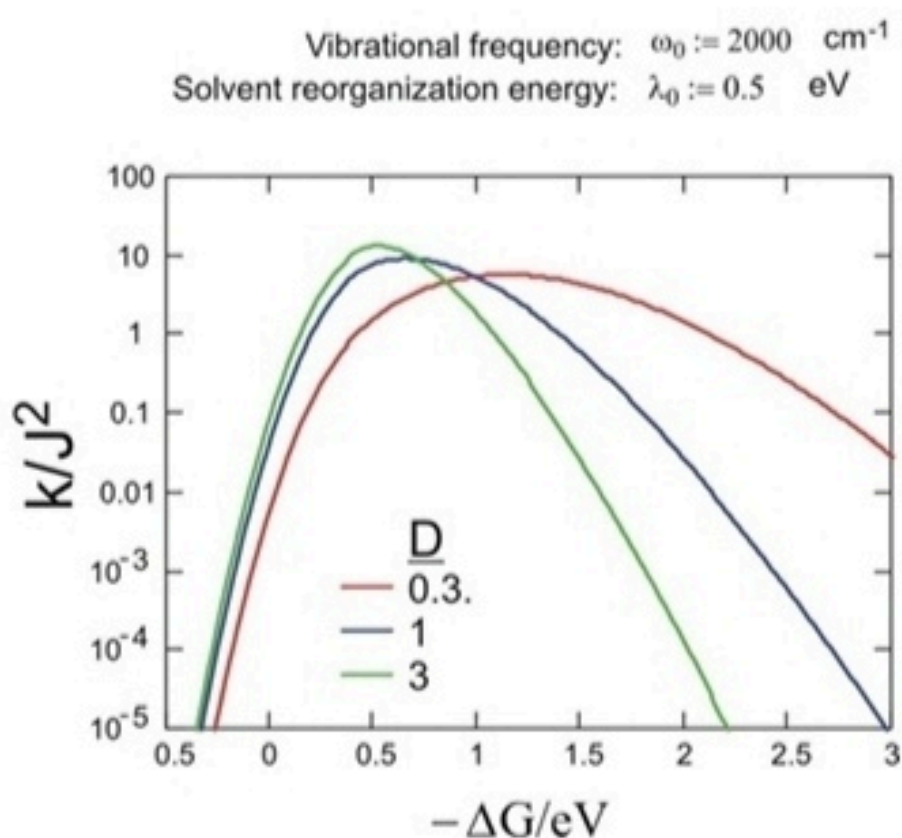
As with electronic spectroscopy, a more general and effective way of accounting for the nuclear motions that mediate the electron transfer process is to describe the coupling weighted density of states as a spectral density. Then we can use coupling to a harmonic bath to describe solvent and/or vibrational contributions of arbitrary form to the transfer event using

$$g(t) = \int_0^{\infty} d\omega \; \rho(\omega)\left[\coth\left(\frac{\beta\hbar\omega}{2} \right)(1-\cos\omega t)+i(\sin\omega t - \omega t) \right]. \tag{12.46}$$