Quantum theory of the electron transfer rate

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PhD Course
CNR NANO S3
Modena
May 21-23 2012

Application of Fermi's golden rule to the linear electron-phonon model

Total Hamilronian (elec+ osc) in the Born-Oppenheimer approximation with a quantum harmonc osc.

States of total system (el+osc)

$$|el-vi\rangle = |el\rangle \otimes |vi\rangle$$

$$\hat{H} = \frac{\hat{P}_R^2}{2M} \otimes \hat{I}^{el} + \hat{H}^{BO}\left(\hat{R}\right)$$

$$\hat{H}^{BO}\left(\hat{R}\right) = E_D^{BO}\left(\hat{R}\right)|D\rangle\langle D| + E_A^{BO}\left(\hat{R}\right)|A\rangle\langle A|$$
$$+ \ \hat{I}^{vi} \otimes T_{DA}\left(|D\rangle\langle A| + |A\rangle\langle D|\right)$$

$$E_D^{BO}\left(\hat{R}\right) = E_{D(\min)}^{BO} + \frac{k}{2}\left(\hat{R} - R^D\right)^2 \qquad E_A^{BO}\left(\hat{R}\right) = E_{D(\min)}^{BO} + \frac{k}{2}\left(\hat{R} - R^A\right)^2$$

$$\hat{I}^{el} = |D\rangle\langle D| + |A\rangle\langle A| \qquad \hat{I}^{vi} = \sum_n |n\rangle\langle n|$$

$$\hat{H} = +\hat{H}^{(0)} + \hat{V}$$

$$\hat{H}_D^{(0)} = \left\{ \frac{\hat{P}_R^2}{2M} + E_D^{BO}\left(\hat{R}\right) \right\} \left| D \right\rangle \left\langle D \right|$$

$$\hat{H}_A^{(0)} = \left\{ \frac{\hat{P}_R^2}{2M} + E_A^{BO}\left(R\right) \right\} \left| A \right\rangle \left\langle A \right|$$

$$\hat{V} = \hat{I}^{vi} \otimes T_{DA} \left(\left| D \right\rangle \left\langle A \right| + \left| A \right\rangle \left\langle D \right| \right)$$

Eigenstates/eigennvalues of unperturbed Hamiltonian (vibronic states)

$$\hat{H}^{(0)}\left|\psi_k\right\rangle = E_k\left|\psi_k\right\rangle \qquad \left|\psi_k\right\rangle,\ E_k$$

$$\left|\psi_k\right\rangle = \begin{cases}\left|n_D\right\rangle\left|D\right\rangle \\ \left|n_A\right\rangle\left|A\right\rangle\end{cases} \qquad E_k = \begin{cases}E^{BO}_{D(\min)} + \varepsilon_{n_D}, & \varepsilon_{n_D} = \hbar\omega\left(n_D + 1/2\right),\ \ n_D : 0,1,.. \\ E^{BO}_{A(\min)} + \varepsilon_{n_A}, & \varepsilon_{n_A} = \hbar\omega\left(n_A + 1/2\right),\ \ n_A : 0,1,..\end{cases}$$

$$\left\{\frac{\hat{P}_R^2}{2M} + E_D^{BO}(R)\right\}\left|n_D\right\rangle = \left\{E^{BO}_{D(\min)} + \hbar\omega\left(n_D + 1/2\right)\right\}\left|n_D\right\rangle$$

Eigenstate of harm osc with equil pos R^D

$$\left\{\frac{\hat{P}_R^2}{2M} + E_A^{BO}(R)\right\}\left|n_A\right\rangle = \left\{E^{BO}_{D(\min)} + \hbar\omega\left(n_A + 1/2\right)\right\}\left|n_A\right\rangle$$

Eigenstate of harm osc with equil pos R^A

Electron transfer:
Transitions from initial to final el-vib states of system

Initial el-vib state of system

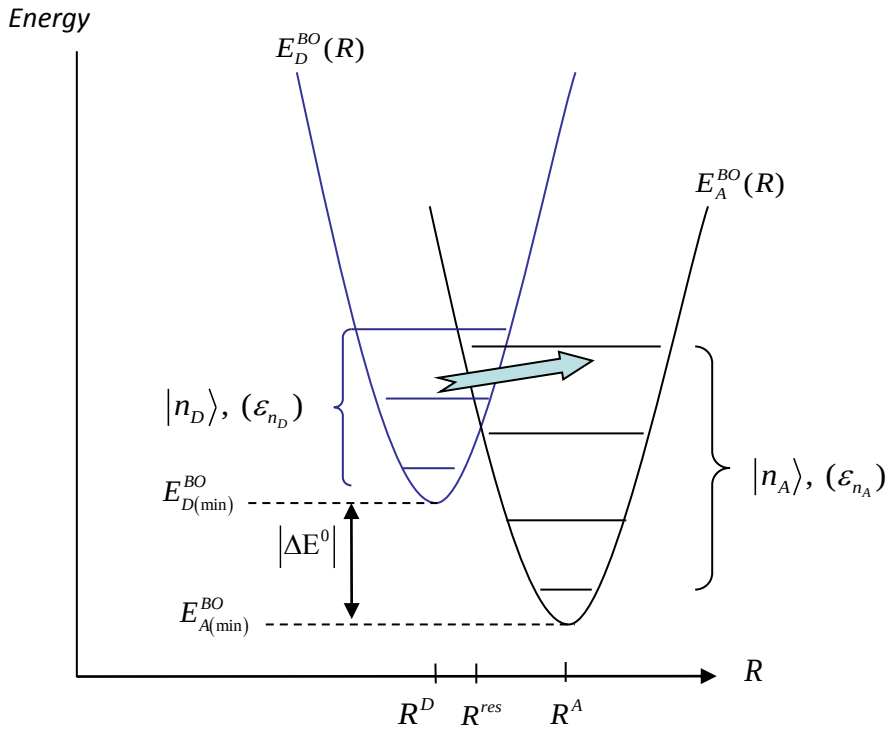
$$|D;n_D\rangle = |D\rangle|n_D\rangle$$

Elec at donor state

Final el-vib state of system

$$|A;n_A\rangle = |A\rangle|n_A\rangle$$

Elec at acceptor state



$|n_D\rangle$ Initial vib state of osc:
Eigenstate of harm osc with equil pos R^D

$|n_A\rangle$ Final vib state of osc :
Eigenstate of harm osc with equil pos R^A

Application of Fermi's golden rule:

Fermi golden rule transition rate between a pair of initial and final vibronic (el-vib)

states:

$$\Gamma_{\psi_{k'}\to\psi_k} = \frac{d}{dt} P_{\psi_{k'}\to\psi_k}(t) \approx \frac{2\pi}{\hbar} \left| \left\langle \psi_{k'} \left| \hat{V} \right| \psi_k \right\rangle \right|^2 \delta\left[E_{k'} - E_k \right]$$

$$\left|\psi_{k'}\right\rangle = \left|n_D\right\rangle \left|D\right\rangle \longrightarrow \left|\psi_k\right\rangle = \left|n_A\right\rangle \left|A\right\rangle$$

$$\hat{V} = \hat{I}^{vi} \otimes T_{DA} \left(\left|D\right\rangle \left\langle A\right| + \left|A\right\rangle \left\langle D\right| \right)$$

Transion matrx element between initial and final vibronic states

$$\left\langle \psi_{k'} \left| \hat{V} \right| \psi_k \right\rangle = \underbrace{\left\langle D \left| \hat{V} \right| A \right\rangle}_{T_{DA}} \left\langle n_D \middle| n_A \right\rangle$$

$$\langle \psi_{k'} | \hat{V} | \psi_k \rangle = T_{DA} \langle n_D | n_A \rangle$$

Donor-to-Acceptor electronic coupling

(Tunneling matrix element)

Overlap between eigenstates of harm osc for the donor and acceptor Born-Openheimer surfaces (Franck-Condon overlap)

$$\langle n_D | n_A \rangle = \int_{-\infty}^{\infty} dR \left\{ X_{n_D}\left(R - R^D\right) \right\}^* X_{n_A}\left(R - R^A\right)$$

$\underline{n_A > n_D}$

$$\langle n_D | n_A \rangle = \exp\left[-\frac{\lambda}{2\hbar\omega} \right] \times \left(\sqrt{\frac{\lambda}{\hbar\omega}} \right)^{(n_A - n_D)} \times \sqrt{\frac{n_D!}{n_A!}} \times \left[L_{n_D}^{(n_A - n_D)}\left(-\frac{\lambda}{\hbar\omega} \right) \right]$$

$\underline{n_D > n_A}$

$$\langle n_D | n_A \rangle = \exp\left[-\frac{\lambda}{2\hbar\omega} \right] \times \left(\sqrt{\frac{\lambda}{\hbar\omega}} \right)^{(n_D - n_A)} \times \sqrt{\frac{n_A!}{n_D!}} \times \left[L_{n_A}^{(n_D - n_A)}\left(-\frac{\lambda}{\hbar\omega} \right) \right]$$

Reorganization energy

$$\lambda = \frac{k}{2}\left(R^A - R^D\right)^2$$

Associated Laguerre polynomial

$$L_p^q(x) = \sum_{k=0}^{p} \frac{(-x)^k}{k!} \left(\frac{(p+q)!}{(q+k)!(p-k)!} \right)$$

Fermi golden rule transition rate

$$\Gamma_{\psi_{k'}\to\psi_k} =$$

$$\frac{2\pi}{\hbar}\left|V_{DA}\right|^2\left|\left\langle n_D\middle|n_A\right\rangle\right|^2\delta\left[\left\{E^{BO}_{D(\min)}+\hbar\omega\left(n_D+1/2\right)\right\}-\left\{E^{BO}_{A(\min)}+\hbar\omega\left(n_A+1/2\right)\right\}\right]$$

Franck-Condon factor

$n_A > n_D$

$$\left|\left\langle n_D\middle|n_A\right\rangle\right|^2 = \exp\left[-\frac{\lambda}{\hbar\omega}\right]\times\left(\frac{\lambda}{\hbar\omega}\right)^{(n_A-n_D)}\times\left(\frac{n_D!}{n_A!}\right)\times\left[L_{n_D}^{(n_A-n_D)}\left(-\frac{\lambda}{\hbar\omega}\right)\right]^2$$

$n_D > n_A$

$$\left|\left\langle n_D\middle|n_A\right\rangle\right|^2 = \exp\left[-\frac{\lambda}{\hbar\omega}\right]\times\left(\frac{\lambda}{\hbar\omega}\right)^{(n_D-n_A)}\times\left(\frac{n_A!}{n_D!}\right)\times\left[L_{n_A}^{(n_D-n_A)}\left(-\frac{\lambda}{\hbar\omega}\right)\right]^2$$

Mean electron transfer rate at temperature T:

Thermally averaged sum of transition rates from all possible initial to all possible final vibronic states

$$k_{DA} = \bar{\Gamma} = \frac{2\pi}{\hbar}\left|V_{DA}\right|^2 \rho_{FC}$$

Thermally averaged Franck-Condon factor

$$\rho_{FC} = \sum_{n_D}\sum_{n_A} \frac{1}{Q_{vib}^{D}} e^{-\hbar\omega\left(n_D+1/2\right)/k_B T} \left|\left\langle n_D \middle| n_A \right\rangle\right|^2 \delta\left[\left\{E_{D(\min)}^{BO} + \hbar\omega\left(n_D+1/2\right)\right\} - \left\{E_{A(\min)}^{BO} + \hbar\omega\left(n_A+1/2\right)\right\}\right]$$

$$Q = \sum_{n_D=0}^{\infty} e^{-\hbar\omega\left(n_D+1/2\right)/k_B T}$$

$$\rho_{FC} =$$

$$\sum_{n_D}\sum_{n_A}\frac{1}{Q_{vib}^{D}}e^{-\hbar\omega\left(n_D+1/2\right)/k_BT}\left|\left\langle n_D\left|n_A\right.\right\rangle\right|^2\delta\left[\left\{E_{D(\min)}^{BO}+\hbar\omega\left(n_D+1/2\right)\right\}-\left\{E_{A(\min)}^{BO}+\hbar\omega\left(n_A+1/2\right)\right\}\right]$$

Homework: Use the fourier transfrom representation of the delta function (as described in the previous lecture) to show that the Franck-Condon factor is the following fourier transform of a "quantum" time- dependent Franck-Condon factor:

$$\rho_{FC}=\tilde{C}_{FC}\left(\omega_{DA}\right)=\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}dt\;e^{i\omega_{DA}t}\;\;C_{FC}\left(t\right)$$

$$\omega_{AD}=\left(E_{A(\min)}^{\mathrm{BO}}-E_{D(\min)}^{\mathrm{BO}}\right)/\hbar$$

$$C_{FC}\left(t\right)=\left\langle e^{i\hat{h}_D\;t/\hbar}e^{-i\hat{h}_A\;t/\hbar}\right\rangle_D=\sum_{n_D}\frac{1}{Q_{vib}^{D}}e^{-\hbar\omega\left(n_D+1/2\right)/k_BT}\left\langle n_D\left|e^{i\hat{h}_D\;t/\hbar}e^{-i\hat{h}_A\;t/\hbar}\right|n_D\right\rangle$$

Quantum thermal average over D BO surface vibrational degrees of freedom

$$\hat{h}_D=\left\{\frac{\hat{P}_R^2}{2M}+\frac{k}{2}\left(\hat{R}-R^D\right)^2\right\}$$

$$\hat{h}_A=\left\{\frac{\hat{P}_R^2}{2M}+\frac{k}{2}\left(\hat{R}-R^A\right)^2\right\}$$

Purely vibrational D & A hamiltonians