

## 2.3 Nonadiabatic Electron Transfer in a Donor–Acceptor Complex

nonadiabatic ET is understood as the charge transition process for which the vibrational motion is much faster than the motion of the transferred electron;  
 bridge mediated long–range ET usually proceeds in the this limit;  
 for the following we introduce a convenient notation of the DA–Hamiltonian

$$H_{DA} = (U_D^{(0)} + H_D)|D\rangle\langle D| + (U_A^{(0)} + H_A)|A\rangle\langle A| + (V_{AD}|A\rangle\langle D| + \text{h.c.}) ;$$

the difference

$$\Delta E = U_D^{(0)} - U_A^{(0)}$$

is known as the *driving force* of the ET;

the transfer coupling between the donor and the acceptor will be accounted for in lowest order of perturbation theory ;

general rate formula

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \sum_{M,N} f_{DM} |V_{DM,AN}|^2 \delta(E_{DM} - E_{AN}) ;$$

we neglect any dependence of the transfer integral  $V_{DA}$  on the vibrational coordinates (Condon–like approximation) and may write

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |V_{DA}|^2 \mathcal{D}_{\text{ET}} ;$$

note the introduction of

$$\mathcal{D}_{\text{ET}} = \sum_{M,N} f_{DM} |\langle \chi_{DM} | \chi_{AN} \rangle|^2 \delta(E_{DM} - E_{AN}) ;$$

this expression can be understood as combined thermal averaged and Franck–Condon weighted density of states (DOS);

### 2.3.1 High–Temperature Case

high–temperature limit:  $k_B T \gg \hbar \omega_\xi$ ;

if this relation holds for all vibrational modes  $\xi$ , it is possible to describe the vibrational dynamics in the framework of classical physics;

use of the PES  $U_m(q)$  ( $q \equiv \{q_\xi\}$ ) for the electron at the donor or acceptor site ( $m = D, A$ );

in standard experimental situations only an average with respect to a large number of identical DA complexes is of interest;

it is replaced by an ensemble average with respect to the thermal equilibrium distribution function;

the following rate expression is obtained:

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \int dq f_D(q) |V_{DA}|^2 \delta(U_D(q) - U_A(q)) ;$$

in the  $\delta$ -function the kinetic energy cancels and the distribution function reduces to

$$f_D(q) = \frac{1}{Z} e^{-U_D(q)/k_B T} ;$$

if parabolic PES are used, an analytical expression for the ET rate can be obtained; case of a single coordinate  $q$  oscillating with frequency  $\omega_{\text{vib}}$ ;

$$\begin{aligned} U_D(q) - U_A(q) &= U_D^{(0)} - U_A^{(0)} + \frac{\omega_{\text{vib}}^2}{2} \left( (q - q^{(D)})^2 - (q - q^{(A)})^2 \right) \\ &= \Delta E - \omega_{\text{vib}}^2 (q^{(D)} - q^{(A)})q + \frac{\omega_{\text{vib}}^2}{2} (q^{(D)2} - q^{(A)2}) ; \end{aligned}$$

the argument of the delta function is linear with respect to  $q$  and vanishes at

$$q^* = \frac{\Delta E + \frac{\omega_{\text{vib}}^2}{2} (q^{(D)2} - q^{(A)2})}{\omega_{\text{vib}}^2 (q^{(D)} - q^{(A)})} ;$$

this value of  $q$  defines the crossing point of both PES; thermal distribution reads

$$f_D(q) = \sqrt{\frac{\omega_{\text{vib}}^2}{2\pi k_B T}} \exp \left\{ -\frac{\omega_{\text{vib}}^2 (q - q^{(D)})^2}{2k_B T} \right\} ;$$

the  $q$ -integration results in

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \frac{|V_{DA}|^2}{\sqrt{2\pi k_B T \omega_{\text{vib}}^2 (q^{(D)} - q^{(A)})^2}} \exp \left\{ -\frac{\omega_{\text{vib}}^2 (q^* - q^{(D)})^2}{2k_B T} \right\} ;$$

rate formula represents the activation law for reaching the crossing point  $q = q^*$  between the donor and the acceptor PES;

activation energy is given by

$$E_{\text{act}} = \frac{1}{2} \omega_{\text{vib}}^2 (q^* - q^{(D)})^2 ;$$

this expression can be rewritten to give

$$E_{\text{act}} = \frac{(\Delta E - E_\lambda)^2}{4E_\lambda} ;$$

the quantity

$$E_\lambda = \frac{\omega_{\text{vib}}^2}{2} (q^{(D)} - q^{(A)})^2 ;$$

is the potential energy of the vibrational coordinate which corresponds to the following situation: initially the electron is at the donor and the vibrational coordinate has the value  $q = q^{(D)}$ ; then a sudden change of the electronic state occurs; in order to reorganize the vibrational coordinate (nuclear configuration) to the new equilibrium value  $q^{(A)}$  the energy  $E_\lambda$  has to be removed from the system; this energy is usually called *reorganization energy*; the name *polarization energy* is also common;

rate expression which follows upon introducing  $E_\lambda$  is usually named after R. A. Marcus, who pioneered the theory of ET reactions starting in the 1950s:

$$k_{\text{ET}} = |V_{DA}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} \exp \left\{ -\frac{(\Delta E - E_\lambda)^2}{4E_\lambda k_B T} \right\};$$

expression is valid if we consider not a single but a large number of vibrational coordinates;

the only change concerns the reorganization energy:

$$E_\lambda = \sum_{\xi} \frac{\omega_{\xi}^2}{2} \left( q_{\xi}^{(D)} - q_{\xi}^{(A)} \right)^2;$$

main advantage of the Marcus formula is the description of the complex vibrational dynamics accompanying the electronic transition by a small number of parameters: the transfer coupling  $V_{DA}$ , the driving force  $\Delta E$ , and the reorganization energy  $E_\lambda$ ;

the rate for the back transfer from the acceptor to the donor follows by the interchange of the donor and the acceptor index leading to a change of the sign of  $\Delta E$ :

$$k_{AD} = k_{DA}(-\Delta E) = e^{-\Delta E/k_B T} k_{DA}(\Delta E);$$

the ratio of the backward and forward rate is given by  $\exp\{-\Delta E/k_B T\}$  (detailed balance condition);

let us consider the ET rate in dependence on the driving force  $\Delta E$  of the reaction at a given value of  $V_{DA}$  and  $E_\lambda$ ; three regions of ET appear:

*normal region* of ET;

*activationless case* (increasing  $\Delta E$ ,  $q^*$  moves to the left until the activation energy becomes zero (this regime of ET is observed in the experiment if the rate becomes independent of temperature);

*inverted region* (strong overlap of vibrational wave functions; nuclear tunneling may become important instead of the thermally activated transfer);

ET in the inverted region has been originally proposed by R. A. Marcus in the 1950s, but it could be verified experimentally only in the late 1980s;

### 2.3.2 Low-Temperature Case: Nuclear Tunneling

we suppose that  $k_B T < \hbar \omega_{\xi}$  holds for all vibrational degrees of freedom participating in the ET reaction;

a quantum mechanical description becomes necessary;

we consider the combined thermally averaged and Franck–Condon weighted density of states and rearrange this formula by replacing the  $\delta$ -function by a time-integral

$$\mathcal{D}_{\text{ET}} = \frac{1}{2\pi\hbar} \int dt \sum_{M,N} f_{DM} \langle \chi_{DM} | \chi_{AN} \rangle \langle \chi_{AN} | \chi_{DM} \rangle e^{i(E_{DM} - E_{AN})t/\hbar}$$

this may be rearranged as

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar) = \frac{1}{2\pi\hbar} \int dt e^{i\Delta E t/\hbar} \sum_{M,N} \langle \chi_{DM} | \hat{R}_D e^{iH_D t/\hbar} e^{-iH_A t/\hbar} | \chi_{AN} \rangle \langle \chi_{AN} | \chi_{DM} \rangle$$

$$= \frac{1}{2\pi\hbar} \int dt e^{i\Delta Et/\hbar} \text{tr}_{\text{vib}} \{ \hat{R}_D e^{iH_D t/\hbar} e^{-iH_A t/\hbar} \}$$

here we introduced the trace

$$\text{tr}_{\text{vib}} \{ \dots \} = \sum_M \langle \chi_{DM} | \dots | \chi_{DM} \rangle$$

and the equilibrium vibrational statistical operator

$$\hat{R}_D = e^{-H_D/k_B T} / \text{tr}_{\text{vib}} \{ e^{-H_D/k_B T} \}$$

## ET Rate for Harmonic Potential Energy Surfaces

we compute  $\mathcal{D}_{\text{ET}}$ , if the two vibrational Hamiltonians  $H_D$  and  $H_A$  describe independent harmonic oscillators (normal mode vibrations);

we use the displacement operator

$$D_m^+ = \exp \left\{ \sum_{\xi} g_m(\xi) (C_{\xi} - C_{\xi}^+) \right\} \equiv \prod_{\xi} D_{\xi}^+(g_m(\xi));$$

the two vibrational Hamiltonian can be generated from the Hamiltonian of a non-shifted oscillator

$$H_m = U_m^{(0)} + D_m^+ H_{\text{vib}} D_m,$$

with

$$H_{\text{vib}} = \sum_{\xi} \hbar \omega_{\xi} (C_{\xi}^+ C_{\xi} + 1/2);$$

the trace formula introduced in  $\mathcal{D}_{\text{ET}}$  can be rewritten as

$$\begin{aligned} & \text{tr}_{\text{vib}} \{ \hat{R}_D e^{iH_D t/\hbar} e^{-iH_A t/\hbar} \} \\ &= e^{i\omega_{DA} t} \text{tr}_{\text{vib}} \{ D_D D_D^+ \hat{R}_{\text{vib}} D_D D_D^+ e^{iH_{\text{vib}} t/\hbar} D_D D_A^+ e^{-iH_{\text{vib}} t/\hbar} D_A D_D^+ \} \\ &= e^{i\omega_{DA} t} \times \text{tr}_{\text{vib}} \{ \hat{R}_{\text{vib}} e^{iH_{\text{vib}} t/\hbar} D_D D_A^+ e^{-iH_{\text{vib}} t/\hbar} D_A D_D^+ \} \\ &= e^{i\omega_{DA} t} \text{tr}_{\text{vib}} \{ \hat{R}_{\text{vib}} e^{iH_{\text{vib}} t/\hbar} D_{DA} e^{-iH_{\text{vib}} t/\hbar} D_{DA}^+ \}; \end{aligned}$$

we introduced the combined displacement operator

$$D_{DA} = D_D D_A^+;$$

using the Heisenberg representation of  $D_{DA}$  which is given by

$$D_{DA}(t) = e^{iH_{\text{vib}} t/\hbar} D_{DA} e^{-iH_{\text{vib}} t/\hbar},$$

the trace formula becomes

$$T(t) = \text{tr}_{\text{vib}} \{ \hat{R}_D e^{iH_D t/\hbar} e^{-iH_A t/\hbar} \} = e^{i\omega_{DA} t} \text{tr}_{\text{vib}} \{ \hat{R}_{\text{vib}} D_{DA}(t) D_{DA}^+(0) \};$$

this is the autocorrelation function of the combined displacement operators taken with respect to the equilibrium of the non-displaced reference oscillators;

there is no coupling among the modes; the vibrational Hamiltonian  $H_{\text{vib}}$  is additive with

respect to the mode index  $\xi$  and the vibrational state  $|N\rangle$  factorizes into the single oscillator states  $|N_\xi\rangle$ ; the trace factorizes into single mode traces

$$T(t) = e^{i\omega_{DA}t} \prod_{\xi} T_{\xi}(t) ;$$

to simplify the notation the mode index  $\xi$  will be dropped, and  $\omega_{\xi}$  is replaced by  $\omega_{\text{vib}}$ ;

$$D_{DA} = D(g_D) D^+(g_A) = D(g_D - g_A) = D(\Delta g) ,$$

where  $\Delta g = g_D - g_A$ ;

the time-dependent displacement operator (the single-mode contribution to it) can be written as

$$\begin{aligned} D_{DA}(t) &= D(\Delta g; t) = e^{i\omega_{\text{vib}}C^+Ct} D(\Delta g) e^{-i\omega_{\text{vib}}C^+Ct} \\ &= \exp \left\{ -\Delta g (C e^{-i\omega_{\text{vib}}t} - C^+ e^{i\omega_{\text{vib}}t}) \right\} ; \end{aligned}$$

the single-mode contribution to the trace reads ( $\mathcal{Z}$  is the single-mode partition function)

$$T_{\xi}(t) = \frac{1}{\mathcal{Z}} \sum_N \langle N | e^{-\hbar\omega_{\text{vib}}N/k_{\text{B}}T} D(\Delta g; t) D^+(\Delta g; 0) | N \rangle ;$$

before proceeding further we calculate the vibrational overlap expression for two arbitrary electronic states

$$\langle \chi_{mM} | \chi_{nN} \rangle = \langle M | D(g_m) D^+(g_n) | N \rangle ;$$

$|N\rangle$  and  $|M\rangle$  are the non-shifted states; we make use of the operator identity

$$e^{\alpha(A+B)} = e^{\alpha A} e^{\alpha B} e^{-\alpha^2[A,B]/2} ,$$

which holds if  $[A, B]$  commutes with  $A$  and  $B$  ( $\alpha$  is some parameter); we obtain

$$D(g_m) D^+(g_n) = D(\Delta g_{mn}) = e^{\Delta g_{mn} C^+} e^{-\Delta g_{mn} C} e^{-\Delta g_{mn}^2/2} ,$$

with  $\Delta g_{mn} = g_m - g_n$ ;

the action of the exponential operator on the oscillator states is calculated using a Taylor expansion

$$e^{-\Delta g_{mn} C} |N\rangle = \sum_{n=0}^N \frac{(-\Delta g_{mn})^n}{n!} C^n |N\rangle = \sum_{n=0}^N \frac{(-\Delta g_{mn})^n}{n!} \sqrt{\frac{N!}{(N-n)!}} |N-n\rangle ;$$

the matrix elements follow as

$$\begin{aligned} \langle \chi_{mM} | \chi_{nN} \rangle &= e^{-(\Delta g_{mn})^2/2} \sum_{i=0}^M \sum_{j=0}^N \frac{(-1)^j (\Delta g_{mn})^{i+j}}{i! j!} \\ &\times \sqrt{\frac{M! N!}{(M-i)! (N-j)!}} \delta_{M-i, N-j} ; \end{aligned}$$

the elements which are diagonal in the vibrational quantum number can be further simplified

$$\langle \chi_{mN} | \chi_{mN} \rangle = e^{-(\Delta g_{mn})^2/2} \sum_{j=0}^N \frac{(-1)^j (\Delta g_{mn})^{2j}}{j!^2} \frac{N!}{(N-j)!}$$

$$= e^{-(\Delta g_{mn})^2/2} L_N((\Delta g_{mn})^2) ,$$

where  $L_N(x)$  is a Laguerre polynomial;

now let us further calculate the trace expression; we introduce

$$\mathcal{M}(N) = \langle N | D(\Delta g; t) D^+(\Delta g; 0) | N \rangle = \langle N | e^{-\alpha(t)C + \alpha^*(t)C^+} e^{\alpha(0)C - \alpha^*(0)C^+} | N \rangle ,$$

with

$$\alpha(t) = \Delta g \exp(-i\omega_{\text{vib}}t) ;$$

we can write

$$\begin{aligned} \mathcal{M}(N) &= \langle N | e^{-|\alpha(t)|^2/2} e^{\alpha^*(t)C^+} e^{-\alpha(t)C} e^{-|\alpha(0)|^2/2} e^{-\alpha^*(0)C^+} e^{\alpha(0)C} | N \rangle \\ &= e^{-\frac{1}{2}(|\alpha(t)|^2 + |\alpha(0)|^2)} \times \langle N | e^{\alpha^*(t)C^+} e^{\alpha(t)C} e^{-\alpha^*(0)C^+} e^{-\alpha(0)C} | N \rangle \\ &= e^{-\frac{1}{2}(|\alpha(t)|^2 + |\alpha(0)|^2 - 2\alpha(t)\alpha^*(0))} \times \langle N | e^{(\alpha^*(t) - \alpha^*(0))C^+} e^{-(\alpha(t) - \alpha(0))C} | N \rangle ; \end{aligned}$$

we introduce the abbreviation

$$\Delta\alpha(t) = \alpha(t) - \alpha(0) = \Delta g(\exp(-i\omega_{\text{vib}}t) - 1) ,$$

and take into account that

$$|\alpha(t)|^2 + |\alpha(0)|^2 - 2\alpha(t)\alpha^*(0) = |\Delta\alpha(t)|^2 - 2i \text{Im}(\alpha(t)\alpha^*(0)) ;$$

we obtain the normal ordering of the original matrix elements in the trace formula

$$\langle N | D(\Delta g; t) D^+(\Delta g; 0) | N \rangle = \exp \left\{ -|\Delta\alpha|^2/2 - i \text{Im}(\alpha^*(t)\alpha(0)) \right\} \langle N | e^{\Delta\alpha^*C^+} e^{-\Delta\alpha C} | N \rangle ;$$

it gives

$$T_\xi(t) = (1 - e^{-\hbar\omega_{\text{vib}}/k_{\text{B}}T}) e^{-z/2 - i \text{Im}(\alpha^*(t)\alpha(0))} \sum_{N=0}^{\infty} e^{-\hbar\omega_{\text{vib}}N/k_{\text{B}}T} L_N(z) ;$$

note the introduction of  $z = |\Delta\alpha(t)|^2$ ;

the relation between the Laguerre polynomials and their generating function reads

$$\sum_{N=0}^{\infty} \lambda^N L_N(z) = \frac{1}{1-\lambda} e^{-\lambda z/(1-\lambda)} \quad (|\lambda| < 1) ;$$

it results in

$$T_\xi(t) = \exp E_\xi(t) ,$$

with

$$E_\xi(t) = -z/2 - i \text{Im}(\alpha^*(t)\alpha(0)) - \frac{e^{-\hbar\omega_{\text{vib}}/k_{\text{B}}T}}{1 - e^{-\hbar\omega_{\text{vib}}/k_{\text{B}}T}} z ;$$

the Bose–Einstein distribution  $n(\omega_{\text{vib}})$  allows us to rewrite the last term of the exponent

$$\begin{aligned} E_\xi(t) &= -z/2 - i \text{Im} \alpha^*(t)\alpha(0) - n(\omega_{\text{vib}})z \\ &= -\frac{1}{2}(1 + 2n(\omega_{\text{vib}}))\Delta g^2(2 - e^{i\omega_{\text{vib}}t} - e^{-i\omega_{\text{vib}}t}) - \frac{1}{2}\Delta g^2(e^{i\omega_{\text{vib}}t} - e^{-i\omega_{\text{vib}}t}) \end{aligned}$$

$$= \frac{\Delta g^2}{2} \left( 2(1 + n(\omega_{\text{vib}}))(e^{-i\omega_{\text{vib}}t} - 1) + 2n(\omega_{\text{vib}})(e^{i\omega_{\text{vib}}t} - 1) \right) ;$$

the result will be denoted by  $E_\xi(t) = -G_\xi(0) + G_\xi(t)$  with

$$G_\xi(t) = \Delta g^2(\xi) \left[ e^{-i\omega_\xi t}(1 + n(\omega_\xi)) + e^{i\omega_\xi t}n(\omega_\xi) \right] ;$$

the complete trace is the product with respect to the various single-mode contributions  $T_\xi(t)$

$$G(t) = \sum_{\xi} G_\xi(t) ;$$

this *exact* result is used in the definition of the density of states

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar) = \frac{1}{2\pi\hbar} \int dt e^{i\Delta Et/\hbar - G(0) + G(t)} ;$$

again with

$$G(t) = \sum_{\xi} (g_A(\xi) - g_D(\xi))^2 \left[ e^{-i\omega_\xi t}(1 + n(\omega_\xi)) + e^{i\omega_\xi t}n(\omega_\xi) \right] ;$$

### ET Rate for the Case of a Single Harmonic Coordinate

once the function  $G(t)$  is given, a single time integration generates the complete ET rate; to achieve a better understanding of this expression we discuss the limit where only a *single* vibrational mode with frequency  $\omega_{\text{vib}}$  couples to the electronic transition

$$G(t) = \Delta g^2 \left( e^{-i\omega_{\text{vib}}t}(1 + n(\omega_{\text{vib}})) + e^{i\omega_{\text{vib}}t}n(\omega_{\text{vib}}) \right) ;$$

expanding the exponential function yields

$$\exp\{G(t)\} = \sum_{M=0}^{\infty} \frac{1}{M!} \left[ \Delta g^2(1 + n(\omega_{\text{vib}})) \right]^M e^{-iM\omega_{\text{vib}}t} \sum_{N=0}^{\infty} \frac{1}{N!} \left[ \Delta g^2 n(\omega_{\text{vib}}) \right]^N e^{iN\omega_{\text{vib}}t} ;$$

inserting this result into the expression of the combined DOS allows to carry out the time integration for every contribution in the double sum

$$\begin{aligned} \mathcal{D}_{\text{ET}}(\Delta E/\hbar) &= \frac{1}{\hbar} e^{-\Delta g^2(1+2n(\omega_{\text{vib}}))} \sum_{M,N=0}^{\infty} \frac{1}{M!} \left[ \Delta g^2(1 + n(\omega_{\text{vib}})) \right]^M \\ &\times \frac{1}{N!} \left[ \Delta g^2 n(\omega_{\text{vib}}) \right]^N \delta(\Delta E/\hbar - (M - N)\omega_{\text{vib}}) ; \end{aligned}$$

we consider the zero-temperature case

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar)|_{T=0} = \frac{1}{\hbar} e^{-\Delta g^2} \sum_{M=0}^{\infty} \frac{\Delta g^{2M}}{M!} \delta(\Delta E/\hbar - M\omega_{\text{vib}}) ;$$

the ET rate covers a sequence of sharp transitions at  $\Delta E/\hbar - M\omega_{\text{vib}}$  with weighting factors

$$w_M = e^{-\Delta g^2} \frac{\Delta g^{2M}}{M!} ;$$

the weighting factors follow from a so-called *Poisson distribution*;

they become maximal at  $M \approx \Delta g^2$  or, in terms of energies, at  $M\hbar\omega_{\text{vib}} \approx \hbar\omega_{\text{vib}}\Delta g^2$ ;

## Introduction of the Spectral Density

if many vibrational modes couple to the electronic transition, we expect a quasi–continuous spectrum of vibrational frequencies; for such a case it is convenient to introduce the *spectral density*

$$J_{DA}(\omega) = \sum_{\xi} (g_A(\xi) - g_D(\xi))^2 \delta(\omega - \omega_{\xi}) ;$$

we assume that the following representation becomes possible

$$(g_A(\xi) - g_D(\xi))^2 = \kappa(\omega_{\xi}) ,$$

and we note the definition of the density of normal–mode oscillations

$$\mathcal{N}(\omega) = \sum_{\xi} \delta(\omega - \omega_{\xi}) ;$$

accordingly, the spectral density can be written as the coupling–strength weighted density of states

$$J_{DA}(\omega) = \kappa(\omega)\mathcal{N}(\omega) ;$$

the introduction of the spectral density results in

$$G(t) = \int_0^{\infty} d\omega [(1 + n(\omega))e^{-i\omega t} + n(\omega)e^{i\omega t}] J_{DA}(\omega) ;$$

the reorganization energy can be expressed via the spectral density as

$$E_{\lambda} = \hbar \sum_{\xi} \omega_{\xi} (g_D(\xi) - g_A(\xi))^2 = \hbar \int_0^{\infty} d\omega \omega J_{DA}(\omega) ;$$

let us introduce the real and imaginary part of the function  $G(t)$

$$G(t) = G_1(t) - iG_2(t) ,$$

where

$$G_1(t) = \int_0^{\infty} d\omega \cos(\omega t) [1 + 2n(\omega)] J_{DA}(\omega) ,$$

and

$$G_2(t) = \int_0^{\infty} d\omega \sin(\omega t) J_{DA}(\omega) ;$$

according to this separation of  $G(t)$  the density of states reads

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar) = \frac{1}{2\pi\hbar} \int dt e^{i[\Delta E t/\hbar - G_2(t)] + G_1(t) - G_1(0)} ;$$

the imaginary part of  $G(t)$  introduces a shift of the driving force whereas the real part ensures integrability;

at this point it is useful to clarify what approximations will lead to the rate formula of the high–temperature limit; to this end we note that irrespective of the actual frequency



dependence, the spectral density rapidly goes to zero beyond a certain cut-off frequency  $\omega_c$ ; hence in the high-temperature limit we have  $k_B T \gg \hbar \omega_c$ ; this enables us to introduce for all frequencies less than  $\omega_c$  the approximation

$$1 + 2n(\omega) \approx 2k_B T / \hbar \omega \gg 1 ;$$

to utilize this inequality next we use the separation of  $G(t)$  into its real and imaginary part; if  $\omega_c |t| \ll \pi/2$ , the quantity  $\exp\{G(t) - G(0)\}$  rapidly approaches zero since the expression  $\cos \omega t - 1$ , which appears in the exponent, is negative; but for  $\omega_c |t| > \pi/2$  the different contributions to the time integral may interfere destructively; consequently, it is possible to approximate  $G(t)$  in the exponent by the leading expansion terms of the sine and cosine functions (this is known as the short-time expansion); using the definition of the spectral density gives

$$G(t) \approx - \int_0^\infty d\omega \frac{(\omega t)^2}{2} 2 \frac{k_B T}{\hbar \omega} J_{DA}(\omega) - i \int_0^\infty d\omega \omega t J_{DA}(\omega) ;$$

both frequency integrals define the reorganization energy, and the combined density of states determining the ET rate follows as

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar) = \int \frac{dt}{2\pi\hbar} \exp \left\{ i \frac{(\Delta E - E_\lambda)t}{\hbar} \right\} \exp \left\{ - \frac{k_B T E_\lambda t^2}{\hbar^2} \right\} ;$$

the remaining integral is easily calculated as

$$\mathcal{D}_{\text{ET}}(\Delta E/\hbar) = \frac{1}{\sqrt{4\pi k_B T E_\lambda}} \exp \left\{ - \frac{(\Delta E - E_\lambda)^2}{4E_\lambda k_B T} \right\} .$$

the classical (high-temperature) limit of the consequent quantum description of non-adiabatic ET reactions reproduces the Marcus formula;

### 2.3.3 The Mixed Quantum-Classical Case

we consider the case that the ET is coupled to high-frequency intramolecular (quantum) modes and to low-frequency (classical) modes;

assuming a decoupling of both types of DOF the vibrational energies of the quantum modes  $E_\mu$  are supplemented by the vibrational Hamiltonian function  $H_m(q)$  of low-frequency normal modes  $q \equiv \{q_\xi\}$ :

$$H_{\text{DA}} = \sum_{\mu\nu} \left( \delta_{\mu\nu} (E_\mu + H_m(q)) + (1 - \delta_{mn}) V_{\mu\nu} \right) |\Psi_\mu\rangle \langle \Psi_\nu| ;$$

the ET rate describes transitions from a manifold of donor states  $|\phi_D\rangle | \chi_{DM} \rangle$  to many acceptor states  $|\phi_A\rangle | \chi_{AN} \rangle$

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \sum_{M,N} \int dq f_{DM} f_D(q) |V_{DM,AN}|^2 \delta(E_{DM} + U_D(q) - E_{AN} - U_A(q)) ;$$

it follows the multi-channel generalization of the Marcus formula

$$k_{\text{ET}} = \sum_{M,N} f_{DM} k_{DM \rightarrow AN} ,$$

with

$$k_{DM \rightarrow AN} = \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} |V_{DM,AN}|^2 \exp \left\{ -\frac{(\Delta E_{DM,AN} - E_\lambda)^2}{4E_\lambda k_B T} \right\};$$

and with the driving forces

$$\Delta E_{DM,AN} = E_{DM} - E_{AN};$$

we discuss the special case where only the vibrational ground state of the quantum mode is occupied in the reactant state, and we concentrate on a single high-frequency normal mode, i.e.,  $E_{AN} = E_A + \hbar\omega_{\text{intra}}(N + \frac{1}{2}) \equiv E_{A0} + \hbar\omega_{\text{intra}}N$ ; the rate follows as

$$k_{\text{ET}} = \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} |V_{DA}|^2 \sum_{N=0}^{\infty} |\langle \chi_{D0} | \chi_{AN} \rangle|^2 \exp \left\{ -\frac{(\Delta E - \hbar\omega_{\text{intra}}N - E_\lambda)^2}{4E_\lambda k_B T} \right\};$$

here, the reference driving force  $\Delta E \equiv E_{D0} - E_{A0}$  has been introduced; we rewrite the rate using a more explicit expression for the Franck–Condon factor

$$\langle \chi_{D0} | \chi_{AN} \rangle = \frac{1}{\sqrt{N!}} g_{DA}^N e^{-g_{DA}^2/2};$$

furthermore, we replace the shift  $g_{DA}$  of the PES of the intramolecular vibration by  $E_\lambda^{(\text{intra})}/\hbar\omega_{\text{intra}}$ :

$$|\langle \chi_{D0} | \chi_{AN} \rangle|^2 = \frac{1}{N!} \left( \frac{E_\lambda^{(\text{intra})}}{\hbar\omega_{\text{intra}}} \right)^N \exp \left\{ -\frac{E_\lambda^{(\text{intra})}}{\hbar\omega_{\text{intra}}} \right\};$$

the final rate expression reads

$$k_{\text{ET}} = \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} |V_{DA}|^2 \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{E_\lambda^{(\text{intra})}}{\hbar\omega_{\text{intra}}} \right)^N \exp \left\{ -\frac{E_\lambda^{(\text{intra})}}{\hbar\omega_{\text{intra}}} \right\} \exp \left\{ -\frac{(\Delta E - \hbar\omega_{\text{intra}}N - E_\lambda)^2}{4E_\lambda k_B T} \right\};$$