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Electron-Transfer Reactions Involving Two Harmonic Potentials
with a Different Force Constant:
the Zusman approach versus the Spin-boson Model

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Abstract

Two approaches: 1) a generalized spin-boson model with a non-linear spin-boson coupling and 2) the Zusman's stochastic Liouville formalism, are employed to analyze the electron-transfer reactions involving two harmonic potentials with a different force constant. An analytical rate formula, expressed as a convoluted integral of the individual rate kernel for each mode, is derived with full consideration of quantum tunneling effects. For a dominant solvent mode at low frequency, the formula can be reduced to the results of the Zusman's theory, showing asymmetry of the Marcus rate plot between the normal and the inverted regions.

1. Introduction

Most treatments of electron-transfer reactions since the pioneering work of Marcus [1], have assumed an identical shape for the free energy surface of both reactant and product. However, as first pointed out by Marcus [1], this assumption becomes questionable in a system with saturated solvent polarization. If an electric field (E) is so strong that $\mu E/k_B T \geq 1$ for a polar solvent with a dipole moment μ , the Langevin function [2] for the induced polarization is no longer a linear function of $\mu E/k_B$. The local field can be strong if a donor or acceptor has a small radius in a highly polar solvent. For example, in a recent experiments by Barbara et al. [3] in the study of charge recombination between the aromatic cation and the halide anion, they have found a large deviation from the Marcus classical theory which may be due to a highly concentrated excess charge in a small reactant. The problem for a system with two different force constants has been examined by Marcus [4] and many others [5,6]. It was suggested that the system can be treated approximately by using an average force constant $\lambda_{\text{eff}} = 2\lambda_1\lambda_2/(\lambda_1+\lambda_2)$, where λ_1 and λ_2 are the force constants for each parabolic potential surfaces. More recently, Kakitani and Mataga [6] have applied the approach of Förster [7] and Dexter [8], introducing the electron insertion spectrum and the electron removal spectrum so that the electron transfer rate is proportional to the integrated overlap of these two spectra. However, this approximation is invalid [9] if a strong correlation exists between the interactions of the solvent bath with the reactant state and with the product state.

In this work, two approaches are employed: 1) the Zusman's stochastic Liouville formalism and 2) a generalized spin-boson model with a non-linear spin-boson coupling. In

section 2, we will first employ the one-dimensional stochastic Liouville theory to derive an analytical expression for the electron-transfer rate, covering both the nonadiabatic and the solvent-controlled adiabatic regimes. Then, in section 3 we will use an alternative spin-boson approach for full consideration of quantum-tunneling modes. Quantum effects on the reaction rates have been extensively studied [10-21]. In the ordinary spin-boson model [22-27], one assumes a linear interaction between the fictitious spin representing the electronic states and the boson field representing the heat bath. Here a generalized spin-boson model will be introduced by including an additional quadratic coupling between the "spin" and the bath. We shall show that this Hamiltonian is equivalent to two displaced harmonic oscillators with a different force constant in the multi-dimensional reaction coordinate. An analytical rate expression will be derived including the tunneling effects of high frequency quantum modes. The rate formula can be expressed as a convoluted integral of the individual rate kernel for each mode. In the high temperature limit, the quantal rate expression will be shown to be equivalent to the results using the Zusman stochastic Liouville theory [28] for overdamped solvent motion. We would like to show that in a highly polarized medium with saturated polarization, the additional quadratic spin-boson interaction causes a difference in the force constants between the initial and final states. The electron-transfer rate kernel for each mode is shown to be non-Gaussian and asymmetry is expected in the Marcus rate plot between the normal and the inverted regions. The simple concept of using a "collapsed" one-dimensional reaction coordinate to describe reaction in multi-dimensional potential surfaces is no longer valid here because the rate kernel is not a Gaussian for a non-linear medium.

2. The stochastic Liouville theory

A stochastic Liouville approach based on the hybrid Bloch-Smoluchowski equation was proposed by Zusman [28] to describe the electron-transfer reactions at high temperature in a medium with large friction. We will first use this approach to investigate electron-transfer reactions involving two parabolic surfaces with a different force constant. Let us consider a system involving two Marcus potential surfaces with a different force constant. The reactant state $|1\rangle$ and the product state $|2\rangle$ can be assigned a Marcus free-energy parabola in the reaction coordinate as given by

$$\begin{aligned} U_1(x) &= \frac{\lambda_1}{2} x^2 \\ U_2(x) &= \frac{\lambda_2}{2} (x-x_0)^2 - E_g, \end{aligned} \tag{2.1}$$

where λ_1 and λ_2 are the force constants; E_g is the free-energy gap between the bottoms of the second parabola and the first one. The bottom of the first parabola $U_1(x)$ is assumed at 0 and the second one $U_2(x)$ at x_0 . The Zusman equation [28] can be expressed in the Laplace transform with the variable s

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &= i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_1 \hat{\rho}_{11} \\
s \hat{\rho}_{22} &= -i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_2 \hat{\rho}_{22} \\
s \hat{\rho}_{12} &= -i \frac{U_{12}}{\hbar} \hat{\rho}_{12} + i \frac{V_{12}}{\hbar} (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_{12} \hat{\rho}_{12} \\
\hat{\rho}_{21} &= \hat{\rho}_{12}^* ,
\end{aligned} \tag{2.2}$$

where $U_{12}(x)$ is defined as $U_1(x) - U_2(x)$. The initial density matrix at the reactant state $|1\rangle$, $\rho_{11}(0)$, is assumed at thermal equilibrium. The Smoluchowski diffusion operators L_1 , L_2 and L_{12} are given by

$$\begin{aligned}
L_1 &= \frac{1}{\tau_{L1}} \left[1 + x \frac{\partial}{\partial x} \right] + \frac{k_B T}{\lambda_1 \tau_{L1}} \frac{\partial^2}{\partial x^2} \\
L_2 &= \frac{1}{\tau_{L2}} \left[1 + (x - x_0) \frac{\partial}{\partial x} \right] + \frac{k_B T}{\lambda_2 \tau_{L2}} \frac{\partial^2}{\partial x^2} \\
L_{12} &= \frac{1}{2} (L_1 + L_2) ,
\end{aligned} \tag{2.3}$$

where τ_{Lk} , the longitudinal relaxation time on the k -th surface, is a constant in time for a Debye solvent.

Eq. (2.2) can be solved using the Green's function method with details given in the appendix A. As derive in eq. (A.12) in the appendix, one can obtain the following kinetic equation involving only $\hat{\sigma}_k(s)$ which is defined as the overall population on the k -th surface, i.e., $\int dx \hat{\rho}_{kk}(x)$ (for $k=1, 2$),

$$\begin{pmatrix} s+k_{12} & -k_{21} \\ -k_{12} & s+k_{21} \end{pmatrix} \begin{pmatrix} \hat{o}_1(s) \\ \hat{o}_2(s) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2.4)$$

where

$$\begin{aligned} k_{12} = & \frac{2\pi}{\hbar} V_{12}^2 \xi \left[\frac{\rho_{11,eq}(x_{c1})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \right. \\ & \left. + \frac{\rho_{11,eq}(x_{c2})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} \right] \\ k_{21} = & \frac{2\pi}{\hbar} V_{12}^2 \xi \left[\frac{\rho_{22,eq}(x_{c1})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \right. \\ & \left. + \frac{\rho_{22,eq}(x_{c2})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} \right]. \end{aligned} \quad (2.5)$$

where $1/\xi$ is the difference in the slope of the potential surfaces at the crossing as given in eq. (A.4). The crossing points x_{c1} and x_{c2} of two adiabatic potential surfaces $U_1(x)$ and $U_2(x)$ are defined in eq. (A.2) of the appendix A. The adiabaticity factor $f_k(x_c, x_c)$ on the k -th surface can be approximated [25] by $\int [G_k(x_c, x_c; t) - \rho_{kk,eq}(x_c)] dt$ and is given by

$$\begin{aligned}
f_1(x_c, x_0) &= \sqrt{\frac{\lambda_1}{2\pi k_B T}} e^{-\frac{\lambda_1 x_c^2}{2k_B T}} \left[\int_0^\infty dt \frac{1}{\sqrt{1-\Delta_1^2(t)}} \exp\left(\frac{\lambda_1 x_c^2}{k_B T} \frac{\Delta_1(t)}{1+\Delta_1(t)} \right) - 1 \right] \\
f_2(x_c, x_0) &= \sqrt{\frac{\lambda_2}{2\pi k_B T}} e^{-\frac{\lambda_2 (x_c - x_0)^2}{2k_B T}} \left[\int_0^\infty dt \frac{1}{\sqrt{1-\Delta_2^2(t)}} \exp\left(\frac{\lambda_2 (x_c - x_0)^2}{k_B T} \frac{\Delta_2(t)}{1+\Delta_2(t)} \right) - 1 \right],
\end{aligned} \tag{2.6}$$

where $\Delta_1(t) = \exp(-t/\tau_{L1})$ and $\Delta_2(t) = \exp(-t/\tau_{L2})$ for a Debye solvent. For a non-Debye solvent, the expression for $\Delta_k(t)$ is more complicate [29-31]. The electron-transfer rate expression derived in eq. (2.5) contains adiabaticity factors which bridge the nonadiabatic and the solvent-controlled adiabatic regimes. These factors can be evaluated using eq. (2.6) and have been discussed in great details by Rips and Jortner [25]. For nonadiabatic processes, the denominator in eq. (2.5) containing adiabaticity factors can be replaced by one.

We have derived in eq. (2.5) an analytical rate expression for electron-transfer reactions. One can express the rate constant in terms of the free-energy gap E_g , the reorganization energy E_{r1} ($1/2\lambda_1 x_0^2$) and E_{r2} ($1/2\lambda_2 x_0^2$), by substitution of x_{c1} and x_{c2} from eq. (A.2), ξ from eq. (A.4), $\rho_{11,eq}(x_c)$ and $\rho_{22,eq}(x_c)$ from eq. (A.7) into eq. (2.5). Because the force constant for each Marcus parabola can be different, E_{r1} and E_{r2} may not be equal. The rate constant in the nonadiabatic regime can be given by

$$\begin{aligned}
k_{12} = & \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_2 k_B T (1 + \frac{E_s}{E_{r1}} - \frac{E_s}{E_{r2}})}} \exp\left\{-\frac{E_{r1}(E_{r2}-E_s)^2}{k_B T [E_{r2} + \sqrt{E_{r1}E_{r2} + E_s(E_{r2}-E_{r1})}]^2}\right\} \\
& + \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_2 k_B T (1 + \frac{E_s}{E_{r1}} - \frac{E_s}{E_{r2}})}} \exp\left\{-\frac{E_{r1}(E_{r2}-E_s)^2}{k_B T [E_{r2} - \sqrt{E_{r1}E_{r2} + E_s(E_{r2}-E_{r1})}]^2}\right\}.
\end{aligned} \tag{2.7}$$

If x_{c1} and x_{c2} are of the same order of magnitude, both terms in eq. (2.7) are comparable and the rate expression is a sum of two quasi-Gaussian profiles. One may define here $E_r = (E_{r1} + E_{r2})/2$, $\Delta E_r = E_{r1} - E_{r2}$. If $\Delta E_r/E_r$ is very small, i.e., $E_{r1} \approx E_{r2}$, one can show that the second term in eq. (2.7) involves a highly activated process ($\propto \exp(-1/2 \lambda_1 x_{c2}^2/k_B T)$) and is much smaller than the first term ($\propto \exp(-1/2 \lambda_1 x_{c1}^2/k_B T)$). Thus, only the first term representing crossing at x_{c1} is important. Eq. (2.7) can be reduced to the lowest order expansion of $\Delta E_r/E_r$ as

$$\begin{aligned}
k_{12} = & \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_r k_B T [1 - \frac{\Delta E_r}{E_r} (\frac{1}{2} + \frac{E_s}{E_r})]}} \exp\left\{-\frac{(E_r - E_s - \frac{\Delta E_r}{2})^2}{4E_r k_B T [1 - \frac{\Delta E_r}{E_r} (1 + \frac{E_s}{2E_r})]}\right\}.
\end{aligned} \tag{2.8}$$

From the rate expression in eq. (2.8) one can observe the asymmetry between the normal and the inverted regions. If $\Delta E_r < 0$ ($E_{r2} > E_{r1}$), the inverted region (E_s larger than E_{r2}) has a larger radius of curvature and is broader; however, if $\Delta E_r > 0$ ($E_{r2} < E_{r1}$), the inverted region has a smaller radius of curvature and is thus sharper. If $E_{r2} = E_{r1} = E_r$ and $\Delta E_r = 0$, eq. (2.8) can be easily reduced to the well-known symmetric Marcus rate expression.

We have derived here an analytical expression for the electron-transfer rate, covering

both the nonadiabatic and the solvent-controlled adiabatic regimes. The effects of high-frequency intramolecular vibrational modes were not considered here because of the intrinsic high temperature approximation in the Zusman's approach. The quantum tunneling effects will be considered in the next section using the spin-boson model.

3. The generalized spin-boson model

First of all, we shall describe the ordinary linear spin-boson model. The spin-boson Hamiltonian [10-21] for a system consisting of a reactant state $|1\rangle$ and a product state $|2\rangle$ in the electron-transfer reactions can be expressed by

$$H = E_g S_z + 2U_{ex} S_x + \sum_k \left[\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 q_k^2 \right] + \sum_k C_k q_k S_z . \quad (3.1)$$

Here we use a fictitious spin-1/2 operator (S_α) to represent the electronic states $|1\rangle$ and $|2\rangle$ which are eigenstates of S_z with eigenvalues $1/2$ and $-1/2$, respectively. The heat bath is assumed be consisted of an ensemble of harmonic oscillators. The last term describes a linear interaction between the fictitious spin and the boson bath. E_g is the free energy gap between $|1\rangle$ and $|2\rangle$. Except for a trivial constant energy term which can be omitted, eq. (3.1) is equivalent to

$$H = E_g S_z + 2U_{ex} S_x + \sum_k \left[\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 (q_k + 2x_{0,k} S_z)^2 \right] . \quad (3.2)$$

The last term describes two sets of harmonic potential surfaces of identical shape centered at $-x_{0,k}$

and $x_{0,k}$, respectively, in the reaction coordinate of the k -th mode. The linear coupling constant C_k in eq. (3.1) is related to the displacement $x_{0,k}$ by $C_k = 2m_k\omega_k^2x_{0,k}$.

Now we will introduce the non-linear spin-boson model. As illustrated in fig. 1, for two sets of harmonic potentials with a different force constant ($\omega_{a,k}$ for $|1\rangle$ and $\omega_{b,k}$ for $|2\rangle$) the generalized spin-boson Hamiltonian can be defined as

$$H = H_0 + H_I, \quad (3.3)$$

where H_0 is the Hamiltonian for the electronic states and the heat bath, and H_I is for the electronic interaction between $|1\rangle$ and $|2\rangle$. They can be expressed explicitly by

$$\begin{aligned} H_0 &= P H_a + (1-P) H_b \\ H_a &= \frac{1}{2}E_g + \sum_k \frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{a,k}^2(q_k + x_{0,k})^2 \\ H_b &= -\frac{1}{2}E_g + \sum_k \frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{b,k}^2(q_k - x_{0,k})^2 \\ H_I &= 2U_{ex}S_x, \end{aligned} \quad (3.4)$$

where P , the projection operator for state $|1\rangle$, is defined as $\frac{1}{2} + S_z$, and $1-P$, the projection operator for state $|2\rangle$, is defined as $\frac{1}{2} - S_z$. These projection operators satisfy the idempotent relationship, i.e., $P^2 = P$, $(1-P)^2 = 1-P$, and $P(1-P) = 0$. Eqs. (3.3) and (3.4) can be reduced to eq. (3.2) if $\omega_{a,k} = \omega_{b,k}$ for a system with an equal force constant. One can show that the Hamiltonian defined in eq. (3.4) can be transformed into

$$H = E'_g S_z + 2U_{ex} S_x + \sum_k \left[\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 q_k^2 \right] + \sum_k C_k q_k S_z + \sum_k D_k q_k^2 S_z . \quad (3.5)$$

where the effective free energy gap E'_g , the linear and the quadratic coupling constants, C_k and D_k , are related to $\omega_{a,k}$ and $\omega_{b,k}$ by

$$C_k = m_k x_{0,k} \frac{4\omega_{a,k}^2 \omega_{b,k}^2}{\omega_{a,k}^2 + \omega_{b,k}^2}$$

$$D_k = \frac{m_k}{2} (\omega_{a,k}^2 - \omega_{b,k}^2) \quad (3.6)$$

$$E'_g = E_g - \sum_k \frac{m_k}{2} (\omega_{a,k}^2 - \omega_{b,k}^2) \left[\frac{2\omega_{a,k} \omega_{b,k}}{\omega_{a,k}^2 + \omega_{b,k}^2} \right]^2 x_{0,k}^2 .$$

The last term of the generalized spin-boson Hamiltonian in eq. (3.5) shows an additional quadratic coupling, proportional to q_k^2 , between the "spin" and the bath. In showing the equivalence between the Hamiltonians defined in eqs. (3.4) and (3.5), we have again omitted a trivial constant energy term.

It can be shown in eq. (B.7) in the appendix B that if the electronic coupling is weak the nonadiabatic forward rate k_{12} can be expressed by

$$k_{12} = \frac{U_{ex}^2}{\hbar^2 \text{Tr}_B(e^{-\beta H_b})} \int_{-\infty}^{\infty} d\tau \text{Tr}_B(e^{-\frac{i}{\hbar} H_b \tau} e^{\frac{i}{\hbar} (\tau - \beta) H_a}) . \quad (3.7)$$

This formula is derived using only the property of the projection operator without assuming a

specific form of H_a and H_b . The Hamiltonians H_a and H_b in eq. (3.7) are generally non-commutable. To evaluate the trace, Tr_B , over all bath coordinates in the above equation, one can use the following propagator technique. The propagator for a quantum harmonic oscillator is well-known [32] and it is given by

$$\begin{aligned}
& \langle x | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} | x' \rangle \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \exp\left\{-\frac{m\omega}{2\hbar\sinh(\beta\hbar\omega)} [(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx']\right\} \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \exp\left\{-\frac{m\omega}{4\hbar} [(x+x')^2 \tanh(\frac{\beta\hbar\omega}{2}) + (x-x')^2 \coth(\frac{\beta\hbar\omega}{2})]\right\}.
\end{aligned} \tag{3.8}$$

To avoid confusion of notation, we use p and q as operators, and x , x' and x_0 as c-numbers. The propagator for a displaced harmonic oscillator can be obtained by the following unitary transformation

$$\begin{aligned}
\langle x | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2(q+x_0)^2)} | x' \rangle &= \langle x | e^{\frac{1}{\hbar}px_0} e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} e^{-\frac{1}{\hbar}px_0} | x' \rangle \\
&= \langle x+x_0 | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} | x'+x_0 \rangle.
\end{aligned} \tag{3.9}$$

Here we have used the following properties of a translation operator, $\exp(ipx_0/\hbar) q \exp(-ipx_0/\hbar) = q + x_0$, and $\exp(-ipx_0/\hbar) | x' \rangle = | x' + x_0 \rangle$. Consequently, the propagators for the Hamiltonians $p_k^2/2m_k + m_k\omega_{a,k}^2(q_k+x_{0,k})^2/2$ and $p_k^2/2m_k + m_k\omega_{b,k}^2(q_k-x_{0,k})^2/2$ defined in eq. (3.4)

as harmonic oscillators centered at $-x_{0,k}$ and $x_{0,k}$, are given by

$$\begin{aligned}
 G_{a,k}(x_k, x'_k; \beta_1) &\equiv \langle x_k | e^{-\beta_1 [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2]} | x'_k \rangle = \sqrt{\frac{m_k \omega_{a,k}}{2\pi \hbar \sinh(\beta_1 \hbar \omega_{a,k})}} \\
 &\exp\left\{-\frac{m_k \omega_{a,k}}{4\hbar} [(x_k + x'_k + 2x_{0,k})^2 \tanh(\frac{\beta_1 \hbar \omega_{a,k}}{2}) + (x_k - x'_k)^2 \coth(\frac{\beta_1 \hbar \omega_{a,k}}{2})]\right\} \quad (3.10) \\
 G_{b,k}(x_k, x'_k; \beta_2) &\equiv \langle x_k | e^{-\beta_2 [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{b,k}^2 (q_k - x_{0,k})^2]} | x'_k \rangle = \sqrt{\frac{m_k \omega_{b,k}}{2\pi \hbar \sinh(\beta_2 \hbar \omega_{b,k})}} \\
 &\exp\left\{-\frac{m_k \omega_{b,k}}{4\hbar} [(x_k + x'_k - 2x_{0,k})^2 \tanh(\frac{\beta_2 \hbar \omega_{b,k}}{2}) + (x_k - x'_k)^2 \coth(\frac{\beta_2 \hbar \omega_{b,k}}{2})]\right\}.
 \end{aligned}$$

One can show from eqs. (3.7) and (3.10) that

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \prod_k \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_k dx'_k G_{b,k}(x_k, x'_k; \frac{i}{\hbar}\tau) G_{a,k}(x'_k, x_k; \beta - \frac{i}{\hbar}\tau)}{\int_{-\infty}^{\infty} dx_k G_{a,k}(x_k, x_k; \beta)} \quad (3.11)$$

The double integrals over x_k and x'_k can be transformed into integrals over the new axes with $(x_k + x'_k)/\sqrt{2}$ and $(x_k - x'_k)/\sqrt{2}$. The independent integration over each new axis involving a Gaussian can then be carried out easily. One can reduce eq. (3.11) to

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \prod_k \exp \left[- \frac{4m_k \omega_{a,k} \omega_{b,k} x_{0,k}^2 / \hbar}{\omega_{a,k} \coth(\frac{\beta_2 \hbar \omega_{b,k}}{2}) + \omega_{b,k} \coth(\frac{\beta_1 \hbar \omega_{a,k}}{2})} \right] \sqrt{\frac{4\omega_{a,k} \omega_{b,k} \sinh^2(\frac{\beta \hbar \omega_{a,k}}{2})}{(\omega_{a,k}^2 + \omega_{b,k}^2) \sinh(\beta_1 \hbar \omega_{a,k}) \sinh(\beta_2 \hbar \omega_{b,k}) + 2\omega_{a,k} \omega_{b,k} [\cosh(\beta_1 \hbar \omega_{a,k}) \cosh(\beta_2 \hbar \omega_{b,k}) - 1]}} \quad (3.12)$$

where $\Omega = E_g/\hbar$, $\beta_1 = \beta - i\tau/\hbar$, and $\beta_2 = i\tau/\hbar$. A similar expression has also been obtained by Lin in a different study of radiationless transitions [33]. For the special case of equal force constants, i.e., $\omega_{a,k} = \omega_{b,k} = \omega_k$, eq. (3.12) can be reduced to a much simpler expression of Kubo and Toyozawa [34]

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \exp \left\{ - \sum_k \frac{2m_k \omega_k x_0^2}{\hbar} \left[\coth\left(\frac{\beta \hbar \omega_k}{2}\right) (1 - \cos \omega_k \tau) + i \sin \omega_k \tau \right] \right\} . \quad (3.13)$$

This particular formula in eq. (3.13) has been widely used in the analysis of electron or energy transfer processes. One may use the steepest descent method [35] to evaluate eq. (3.12) which can be expressed as

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{-\phi(\tau)}$$

$$\begin{aligned} \phi(\tau) = & -i\Omega\tau + \sum_k \left[\frac{4m_k \omega_{a,k} \omega_{b,k} x_{0,k}^2 / \hbar}{\omega_{a,k} \coth(\frac{\beta_2 \hbar \omega_{b,k}}{2}) + \omega_{b,k} \coth(\frac{\beta_1 \hbar \omega_{a,k}}{2})} - \frac{1}{2} \ln \{ 4\omega_{a,k} \omega_{b,k} \sinh^2(\frac{\beta \hbar \omega_{a,k}}{2}) \} \right. \\ & \left. + \frac{1}{2} \ln \{ (\omega_{a,k}^2 + \omega_{b,k}^2) \sinh(\beta_1 \hbar \omega_{a,k}) \sinh(\beta_2 \hbar \omega_{b,k}) + 2\omega_{a,k} \omega_{b,k} [\cosh(\beta_1 \hbar \omega_{a,k}) \cosh(\beta_2 \hbar \omega_{b,k}) - 1] \} \right] . \end{aligned} \quad (3.14)$$

By expanding $\phi(\tau)$ around the saddle point τ_s where the first derivative $\phi'(\tau_s)$ vanishes, i.e., $\phi(\tau) \approx \phi(\tau_s) + \frac{1}{2} \phi''(\tau_s) (\tau - \tau_s)^2$, the rate expression can then be approximated by

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \sum_s \sqrt{\frac{2\pi}{\phi''(\tau_s)}} e^{-\phi(\tau_s)}, \quad (3.15)$$

where $\phi''(\tau_s)$ is the second derivative of $\phi(\tau)$ at τ_s , and $\sum_s$ denotes the summation over all the saddle points.

4. The high temperature regime

To evaluate the rate expression in eq. (3.14) for an arbitrary spectral distribution of $\omega_{a,k}$ and $\omega_{b,k}$, one has to use a numerical approach, e.g., imaginary time path integral Monte Carlo method of Wolynes [35]. We shall show that a simple relation can be derived if the spectral density is concentrated at very low frequency. In this limit, the harmonic oscillators behave as classical objects and their Hamiltonians H_a and H_b are assumed to be commutable. One has

$$\begin{aligned}
& \langle x_k | e^{-i\frac{\tau}{\hbar}[\frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{b,k}^2(q_k - x_{0,k})^2]} e^{(1-\beta)\frac{\tau}{\hbar}[\frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{a,k}^2(q_k + x_{0,k})^2]} | x_k \rangle \\
&= \langle x_k | e^{-i\frac{\tau}{\hbar}[\frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{b,k}^2(q_k - x_{0,k})^2]} + (1-\beta)\frac{\tau}{\hbar}[\frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{a,k}^2(q_k + x_{0,k})^2]} | x_k \rangle \\
&= e^{i\frac{\tau}{\hbar}[\frac{1}{2}m_k\omega_{a,k}^2(x_k + x_{0,k})^2 - \frac{1}{2}m_k\omega_{b,k}^2(x_k - x_{0,k})^2]} \langle x_k | e^{-\beta[\frac{p_k^2}{2m_k} + \frac{1}{2}m_k\omega_{a,k}^2(q_k + x_{0,k})^2]} | x_k \rangle \\
&= \sqrt{\frac{m_k}{2\pi\beta\hbar^2}} e^{-\left(\beta - i\frac{\tau}{\hbar}\right)\frac{m_k\omega_{a,k}^2}{2}(x_k + x_{0,k})^2 - i\frac{\tau}{\hbar}\frac{m_k\omega_{b,k}^2}{2}(x_k - x_{0,k})^2} .
\end{aligned} \tag{4.1}$$

Using eqs. (3.4) and (4.2), one can reduce eq. (3.13) to

$$\begin{aligned}
k_{12} &= \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \prod_k \int_{-\infty}^{\infty} dx_k \sqrt{\frac{\beta m_k \omega_{a,k}^2}{2\pi}} \\
&\cdot \exp\left\{-\frac{m_k \omega_{a,k}^2}{2}(\beta - i\frac{\tau}{\hbar})(x_k + x_{0,k})^2 - i\frac{\tau}{\hbar}\frac{m_k \omega_{b,k}^2}{2}(x_k - x_{0,k})^2\right\} .
\end{aligned} \tag{4.2}$$

Eq. (4.2) is an approximated form of eq. (3.12) in the high temperature regime.

Evaluation of the integrals over τ and x_k in eq. (4.2) can be done by the following technique. We will first consider a single mode, then extend the technique to multiple modes. Now let us consider the special case of only a single dominant solvent mode and thus the index k can be dropped. The integral over τ in the above equation can be easily carried out and one can show

$$k_{12} = \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} dx \sqrt{\frac{\beta m \omega_a^2}{2\pi}} e^{-\frac{\beta m \omega_a^2}{2}(x+x_0)^2} \cdot 8\pi \hbar \delta[(E_{r,a} - E_{r,b}) \frac{x^2}{x_0^2} + 2(E_{r,a} + E_{r,b}) \frac{x}{x_0} + 4E_g + E_{r,a} - E_{r,b}] , \quad (4.3)$$

where we have defined two kinds of reorganization energy as

$$E_{r,a} = \frac{1}{2} m \omega_a^2 (2x_0)^2$$

$$E_{r,b} = \frac{1}{2} m \omega_b^2 (2x_0)^2 . \quad (4.4)$$

The δ -function in eq. (4.3) can be reduced to

$$\delta[(E_{r,a} - E_{r,b}) \frac{x^2}{x_0^2} + 2(E_{r,a} + E_{r,b}) \frac{x}{x_0} + 4E_g + E_{r,a} - E_{r,b}]$$

$$= \frac{x_0}{4\sqrt{E_{r,a}E_{r,b} + E_g(E_{r,b} - E_{r,a})}} [\delta(x - x_{c1}) + \delta(x - x_{c2})] , \quad (4.5)$$

where x_{c1} and x_{c2} can be understood as the crossing points for the effective Marcus adiabatic potential surfaces, and they are defined as

$$\begin{aligned}
x_{c1} &= x_0 \frac{(E_{r,a} + E_{r,b}) - 2 \sqrt{E_{r,a} E_{r,b} + E_g(E_{r,b} - E_{r,a})}}{E_{r,b} - E_{r,a}} \\
x_{c2} &= x_0 \frac{(E_{r,a} + E_{r,b}) + 2 \sqrt{E_{r,a} E_{r,b} + E_g(E_{r,b} - E_{r,a})}}{E_{r,b} - E_{r,a}} .
\end{aligned} \tag{4.6}$$

The integral in eq. (4.3) involving a δ -function is simple. With the help of eq. (4.5), one can obtain the following formula

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar} U_{\alpha}^2 \frac{1}{\sqrt{4\pi E_{r,b} k_B T (1 + \frac{E_g}{E_{r,a}} - \frac{E_g}{E_{r,b}})}} \exp\left\{ - \frac{E_{r,a}(E_{r,b} - E_g)^2}{k_B T [E_{r,b} + \sqrt{E_{r,a} E_{r,b} + E_g(E_{r,b} - E_{r,a})}]^2} \right\} \\
&+ \frac{2\pi}{\hbar} U_{\alpha}^2 \frac{1}{\sqrt{4\pi E_{r,b} k_B T (1 + \frac{E_g}{E_{r,a}} - \frac{E_g}{E_{r,b}})}} \exp\left\{ - \frac{E_{r,a}(E_{r,b} - E_g)^2}{k_B T [E_{r,b} - \sqrt{E_{r,a} E_{r,b} + E_g(E_{r,b} - E_{r,a})}]^2} \right\} .
\end{aligned} \tag{4.7}$$

This result agrees with our earlier derivation in eq. (2.7) using an alternative based on the Zusman stochastic Liouville theory for overdamped solvent motion in one-dimensional reaction coordinate.

Now we will discuss the case of multiple solvent modes. For many discrete low frequency solvent modes, eq. (4.2) can be expressed as

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\alpha\tau} \prod_{k=1}^N \int_{-\infty}^{\infty} dx_k g_k(\tau, x_k) \quad (4.8)$$

$$g_k(\tau, x_k) = \sqrt{\frac{\beta m_k \omega_{a,k}^2}{2\pi}} \exp\left[-\frac{m_k \omega_{a,k}^2}{2} \left(\beta - i\frac{\tau}{\hbar}\right)(x+x_{0,k})^2 - i\frac{\tau}{\hbar} \frac{m_k \omega_{b,k}^2}{2} (x-x_{0,k})^2\right].$$

One may first carry out the integral over τ and one has

$$\begin{aligned} & \int_{-\infty}^{\infty} d\tau e^{i\alpha\tau} \prod_{k=1}^N g_k(\tau, x_k) \\ &= 2\pi\hbar \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \left(\frac{1}{2\pi\hbar}\right)^N \tilde{g}_1(E_1, x_1) \dots \tilde{g}_N(E_N, x_N) \delta(E_g - E_1 \dots - E_N) \end{aligned} \quad (4.9)$$

$$\tilde{g}_k(E_k, x_k) = \int_{-\infty}^{\infty} d\tau e^{\frac{i}{\hbar} E_k \tau} g_k(\tau, x_k).$$

Using eq. (4.9) one can reduce eq. (4.8) to

$$\begin{aligned} k_{12} &= \frac{2\pi}{\hbar} U_{\alpha}^2 \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \delta(E_g - E_1 \dots - E_N) \\ &\quad \cdot \int_{-\infty}^{\infty} dx_1 \frac{\tilde{g}_1(E_1, x_1)}{2\pi\hbar} \dots \int_{-\infty}^{\infty} dx_N \frac{\tilde{g}_N(E_N, x_N)}{2\pi\hbar} \end{aligned} \quad (4.10)$$

The integral over x_k is very similar to the procedure as in the derivation of eq. (4.7). One can show

$$k_{12} = \frac{2\pi}{\hbar} U_{\text{ex}}^2 \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \delta(E_g - E_1 \dots - E_N) \hat{g}_1(E_1) \dots \hat{g}_N(E_N) \quad (4.11)$$

and

$$\begin{aligned} \hat{g}_k(E_k) &= \int_{-\infty}^{\infty} dx_k \frac{\tilde{g}_k(E_k, x_k)}{2\pi\hbar} \\ &= \frac{1}{\sqrt{4\pi E_{r,b_k} k_B T (1 + \frac{E_k}{E_{r,a_k}} - \frac{E_k}{E_{r,b_k}})}} \exp\left\{-\frac{E_{r,a_k}(E_{r,b_k} - E_k)^2}{k_B T [E_{r,b_k} + \sqrt{E_{r,a_k} E_{r,b_k} + E_k(E_{r,b_k} - E_{r,a_k})}]^2}\right\} \\ &+ \frac{1}{\sqrt{4\pi E_{r,b_k} k_B T (1 + \frac{E_k}{E_{r,a_k}} - \frac{E_k}{E_{r,b_k}})}} \exp\left\{-\frac{E_{r,a_k}(E_{r,b_k} - E_k)^2}{k_B T [E_{r,b_k} - \sqrt{E_{r,a_k} E_{r,b_k} + E_k(E_{r,b_k} - E_{r,a_k})}]^2}\right\}, \end{aligned} \quad (4.12)$$

where two kinds of reorganization energy for the k-th mode are defined as

$$\begin{aligned} E_{r,a_k} &= \frac{1}{2} m_k \omega_{a,k}^2 (2x_{0,k})^2 \\ E_{r,b_k} &= \frac{1}{2} m_k \omega_{b,k}^2 (2x_{0,k})^2. \end{aligned} \quad (4.13)$$

Eq. (4.12) is identical to the result in eq. (2.7) derived earlier using the Zusman approach for one-dimensional reaction coordinate. The final rate expression in eq. (4.11), however, is more general which considers a multi-dimensional reaction coordinate whereas in the stochastic Liouville

approach only one-dimensional reaction coordinate is considered.

5. Discussion and Conclusions

In this work we have examined the electron transfer reactions involving multi-mode harmonic potentials with distinctive initial and final state force constants. We have employed two different approaches using the semi-classical Zusman formalism and the generalized spin-boson model. In the Zusman approach, one is dealing with classical overdamped solvent motion in one dimensional reaction coordinate. In the spin-boson model, the low frequency solvent and high frequency intramolecular motion are treated quantum mechanically. The concept of "collapsing" multi-dimensional reaction coordinate $\int$ into one effective reaction coordinate in the classical Marcus theory or Zusman approach is very special for an unsaturated medium with a linear spin-boson interaction. As shown by Kuharski et al. [36] in molecular dynamics simulation of electron transfer in aqueous ferrous-ferric exchange reactions, they have obtained simple parabolic free energy surfaces characterized by one effective reaction coordinate. Their work beautifully demonstrates the simple Marcus scheme using a "collapsed" reaction coordinate. However, such a simplified description with one "collapsed" reaction coordinate is valid only if every rate kernel $g_k(E_k)$ in eq. (4.12) for each mode has a pure Gaussian form. The resultant rate expression in eq. (4.11) as a convolution of many Gaussian rate kernels remains as a Gaussian. If quantum tunneling effects for high frequency modes are important, even if the force constants are equal, the associated rate kernel is non-Gaussian. In this work, we would like to add that in a medium with saturated polarization the rate kernel is also non-Gaussian. Because of the quadratic spin-boson interaction, the force constants are significantly different between the initial and final states.

Consequently, one should expect asymmetry in the Marcus rate plot between the normal and the inverted regions. In this work, we have shown the equivalence between eq. (4.12) for individual rate kernel $g_k(E_k)$ using the generalized spin-boson model in the high temperature limit and eq. (2.7) from the Zusman approach. This indicates that the Zusman stochastic Liouville theory is more restrictive and is valid if there is only one solvent mode. For multiple modes whether of solvent or intramolecular motion, the rate expression is a convoluted integral of the rate kernel for each individual mode. In an unsaturated linear multi-mode medium, one may still use the Zusman formalism with one "collapsed" effective reaction coordinate, the generalization is not true for saturated non-linear multi-mode medium.

In section 3, we have applied a generalized spin-boson model with a quadratic coupling between the "spin" and the bath. Unlike the ordinary spin-boson model with a linear coupling, this generalized model is equivalent to a Hamiltonian with the electronic states coupled to two sets of displaced harmonic oscillators with a different force constant. By using the propagator technique for a quantum harmonic oscillator, we have derived in eq. (3.14) an analytical formula for nonadiabatic electron-transfer rate. This general expression of the rate constant has considered the tunneling effects of the high frequency quantum modes. The time integral can be easily carried out by numerical method for any given spectral distribution of the heat bath. We have also shown that, in the high temperature limit, the formula can be reduced to a simple form if only one single low frequency solvent mode dominates. The rate expression in eq. (4.7) consists of two quasi-Gaussian functions which correspond to the transitions at two crossing points of the effective Marcus potential surfaces. This particular result agrees with earlier derivation using the one-

dimensional stochastic Liouville theory for overdamped solvent motion. For multiple discrete modes at low frequency, the rate constant can be expressed in eqs. (4.11) and (4.12) as a convolution of these quasi-Gaussian functions for each individual mode. The convoluted integral can be simplified only if eq. (4.12) has a pure Gaussian form which exists for the classical Marcus theory for two parabolas with an identical force constant.

Appendix A

As argued by Zusman [28] the evolution of the off-diagonal elements $\hat{\rho}_{12}$ and $\hat{\rho}_{21}$ involves fast oscillation and the diffusion operator L_{12} can be neglected here. One can solve for $\hat{\rho}_{12}$ and $\hat{\rho}_{21}$ in terms of $\hat{\rho}_{11}$ and $\hat{\rho}_{22}$. Eq. (2.2) can then be reduced to

$$\begin{aligned} s \hat{\rho}_{11} - \rho_{11}(0) &= - \frac{2s}{\hbar^2 s^2 + U_{12}^2} V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \\ s \hat{\rho}_{22} &= \frac{2s}{\hbar^2 s^2 + U_{12}^2} V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} , \end{aligned} \quad (\text{A.1})$$

One may notice that $2s/(\hbar^2 s^2 + U_{12}(x)^2)$ in the above equation can be approximated by a δ -function $2\pi\delta(U_{12}(x))/\hbar$ which is important only around the points where $U_{12}(x)$ vanishes. Two roots, x_{c1} and x_{c2} , can be found for the quadratic equation of $U_{12}(x) = \frac{1}{2}\lambda_1 x^2 - \frac{1}{2}\lambda_2 (x-x_0)^2 + E_g = 0$ and they are given by

$$\begin{aligned}
x_{c1} &= \frac{\lambda_2 x_0}{\lambda_2 - \lambda_1} - \sqrt{\frac{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)}{(\lambda_2 - \lambda_1)^2}} \\
x_{c2} &= \frac{\lambda_2 x_0}{\lambda_2 - \lambda_1} + \sqrt{\frac{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)}{(\lambda_2 - \lambda_1)^2}} .
\end{aligned}
\tag{A.2}$$

If $\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1) \geq 0$, these two roots are real numbers and represent the physical crossing points of two surfaces $U_1(x)$ and $U_2(x)$. Because the transition is dominant at the crossing points, $2s/(\hbar^2 s^2 + U_{12}(x)^2)$ in eq. (A.1) can be approximated by expansion around x_{c1} and x_{c2} . One has

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &\sim - \left[\frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_1^2}(x-x_{c1})^2} + \frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_2^2}(x-x_{c2})^2} \right] V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \\
s \hat{\rho}_{22} &= \left[\frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_1^2}(x-x_{c1})^2} + \frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_2^2}(x-x_{c2})^2} \right] V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} .
\end{aligned}
\tag{A.3}$$

The factors $1/\xi_1$ and $1/\xi_2$ are the difference in the slope of two potential surfaces at the crossing points, i.e., $|U_{12}'(x_{c1})|$ and $|U_{12}'(x_{c2})|$, respectively. They are found to be identical as given by

$$\frac{1}{\xi} = \sqrt{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)} .
\tag{A.4}$$

By using the approximation of $2s/(\hbar^2 s^2 + (x-x_{c\pm})^2/\xi^2)$ by a δ -function $2\pi\xi\delta(x-x_{c\pm})/\hbar$, eq. (A.3) can be reduced to

$$s \hat{\rho}_{11} - \rho_{11}(0) = - \frac{2\pi}{\hbar} V_{12}^2 \xi [\delta(x-x_{c1}) + \delta(x-x_{c2})] (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \quad (A.5)$$

$$s \hat{\rho}_{22} = \frac{2\pi}{\hbar} V_{12}^2 \xi [\delta(x-x_{c1}) + \delta(x-x_{c2})] (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} .$$

The assumption of a rate equation involving only the diagonal element and a δ -function coupling, $V_{12}^2 \delta(x-x_c)$, in the previous work [31] is not necessary. It comes naturally from our treatment of the full eq. (2.2) involving both the diagonal and the off-diagonal elements. The difference in the slope of the potential at the crossing point as given by $1/\xi$ is now also a function of E_k . In the ordinary Marcus theory, it is related only to the reorganization energy.

The above equation can be solved by the Green's function method [25]. The Green's functions $G_1(x, x'; t)$ and $G_2(x, x'; t)$ for the Smoluchowski diffusion equation on a parabolic surface are well known and they are given by [25,31]

$$G_1(x, x'; t) = \sqrt{\frac{\lambda_1}{2\pi k_B T (1 - e^{-2\psi\tau_{12}})}} \exp\left\{-\frac{\lambda_1 [x - x' e^{-\psi\tau_{12}}]^2}{2k_B T (1 - e^{-2\psi\tau_{12}})}\right\} \quad (A.6)$$

$$G_2(x, x'; t) = \sqrt{\frac{\lambda_2}{2\pi k_B T (1 - e^{-2\psi\tau_{12}})}} \exp\left\{-\frac{\lambda_2 [x - x_0 - (x' - x_0)e^{-\psi\tau_{12}}]^2}{2k_B T (1 - e^{-2\psi\tau_{12}})}\right\} .$$

At $t=0$ both $G_1(x, x'; 0)$ and $G_2(x, x'; 0)$ are given by $\delta(x-x')$. As time approaches infinity, $G_k(x, x'; \infty)$ is given by the Boltzmann distribution $\rho_{kk,eq}(x)$ as

$$\begin{aligned}
\rho_{11,\text{eq}}(x) &= \sqrt{\frac{\lambda_1}{2\pi k_B T}} e^{-\frac{\lambda_1 x^2}{2k_B T}} \\
\rho_{22,\text{eq}}(x) &= \sqrt{\frac{\lambda_2}{2\pi k_B T}} e^{-\frac{\lambda_2 (x-x_0)^2}{2k_B T}} .
\end{aligned} \tag{A.7}$$

The Laplace transform of the Green's function satisfies the following equation

$$(s - L_k) \hat{G}_k(x, x') = \delta(x - x') , \quad k = 1, 2 . \tag{A.8}$$

With the Green's function method, one can show from eq. (A.5)

$$\begin{aligned}
\hat{\rho}_{11}(x) &= \frac{1}{s} \rho_{11,\text{eq}}(x) - \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_1(x, x_{01}) (\hat{\rho}_{11}(x_{01}) - \hat{\rho}_{22}(x_{01})) \\
&\quad - \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_1(x, x_{02}) (\hat{\rho}_{11}(x_{02}) - \hat{\rho}_{22}(x_{02})) \\
\hat{\rho}_{22}(x) &= \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_2(x, x_{01}) (\hat{\rho}_{11}(x_{01}) - \hat{\rho}_{22}(x_{01})) \\
&\quad + \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_2(x, x_{02}) (\hat{\rho}_{11}(x_{02}) - \hat{\rho}_{22}(x_{02})) .
\end{aligned} \tag{A.9}$$

The overall populations $\hat{\sigma}_1(s)$ and $\hat{\sigma}_2(s)$ on each surface, defined as $\int dx \hat{\rho}_{kk}(x)$ (for $k=1, 2$), can be obtained by integrating $\hat{\rho}_{kk}(x)$ in eq. (A.9) over x , and they are given by

$$s\hat{\sigma}_1(s) - 1 = - \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) - \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})) \quad (\text{A.10})$$

$$s\hat{\sigma}_2(s) = \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) + \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})) .$$

One can show that $G_k(x, x')$ can be approximated by $\rho_{kk,eq}(x)/s + f_k(x, x')$ [29]. With the help of this relation and eq. (A.9), one can evaluate $\hat{\rho}_{kk}(x)$ at x_{c1} and x_{c2} , the crossing points. One has

$$\begin{aligned} \hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1}) &= \frac{\rho_{11,eq}(x_{c1}) \hat{\sigma}_1(s) - \rho_{22,eq}(x_{c1}) \hat{\sigma}_2(s)}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \\ \hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2}) &= \frac{\rho_{11,eq}(x_{c2}) \hat{\sigma}_1(s) - \rho_{22,eq}(x_{c2}) \hat{\sigma}_2(s)}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} . \end{aligned} \quad (\text{A.11})$$

In deriving the above relation, we have assumed that the crossing points are generally far apart except the special case with $\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_1 - \lambda_2) = 0$. Thus, the cross terms such as $f_1(x_{c1}, x_{c2})$ and $f_2(x_{c2}, x_{c1})$ are negligible comparing to $f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})$ and $f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})$.

With help from eqs. (A.10) and (A.11), one can derive the following kinetic equation in Laplace transformation involving only $\hat{\sigma}_k(s)$, the population on the reactant ($k=1$) or the product surfaces ($k=2$),

$$\begin{pmatrix} s+k_{12} & -k_{21} \\ -k_{12} & s+k_{21} \end{pmatrix} \begin{pmatrix} \hat{\sigma}_1(s) \\ \hat{\sigma}_2(s) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (\text{A.12})$$

Appendix B

Using the interaction representation, one can describe the time evolution of the density matrix by

$$\frac{\partial \tilde{\rho}}{\partial t} = \frac{i}{\hbar} [\tilde{\rho}, \tilde{H}_I(t)], \quad (\text{B.1})$$

and

$$\tilde{H}_I(t) = e^{\frac{i}{\hbar} \hat{H}_0 t} \hat{H}_I(t) e^{-\frac{i}{\hbar} \hat{H}_0 t}. \quad (\text{B.2})$$

To derive a rate equation involving only the electronic states $|1\rangle$ and $|2\rangle$, one can define a 2x2 reduced density matrix $\tilde{\sigma}(t)$ for these states. It is defined as the trace of $\tilde{\rho}$, i.e., $\text{Tr}_B(\tilde{\rho}(t))$, by taking an ensemble average over all the bath coordinates. It can be shown that eq. (B.1) can be transformed into the following integrodifferential equation

$$\frac{d\tilde{\sigma}}{dt} = - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \{ [\tilde{H}_I(t), [\tilde{H}_I(t-\tau), \sigma_B \tilde{\sigma}(t-\tau)]] \}, \quad (\text{B.3})$$

assuming H_I is a weak perturbation and the density matrix for the bath (σ_B) is given by $\exp(-\beta H_B)/\text{Tr}_B(\exp(-\beta H_B))$ where $\beta = 1/k_B T$. One can show that $\tilde{H}_I(t)$ is given by

$$\tilde{H}_I(t) = U_{\text{ex}} \begin{pmatrix} 0 & e^{\frac{i}{\hbar} H_A t} e^{-\frac{i}{\hbar} H_B t} \\ e^{\frac{i}{\hbar} H_B t} e^{-\frac{i}{\hbar} H_A t} & 0 \end{pmatrix}. \quad (\text{B.4})$$

By substitution of eq. (B.4) into eq. (B.3), one can derive the following kinetic equation for the populations $\tilde{\sigma}_{11}$ and $\tilde{\sigma}_{22}$

$$\begin{aligned} \frac{d\tilde{\sigma}_{11}}{dt} = & - \frac{U_{\text{ex}}^2}{\hbar^2} \int_0^t d\tau \left[\text{Tr}_B(e^{-\frac{i}{\hbar} H_B \tau} e^{\frac{i}{\hbar} H_A \tau} \sigma_B) + \text{Tr}_B(e^{\frac{i}{\hbar} H_B \tau} e^{-\frac{i}{\hbar} H_A \tau} \sigma_B) \right] \tilde{\sigma}_{11}(t-\tau) \\ & + \frac{U_{\text{ex}}^2}{\hbar^2} \int_0^t d\tau \left[\text{Tr}_B(e^{\frac{i}{\hbar} H_B \tau} e^{-\frac{i}{\hbar} H_A \tau} e^{\frac{i}{\hbar} H_A(t-\tau)} e^{-\frac{i}{\hbar} H_B(t-\tau)} \sigma_B) + \right. \\ & \left. \text{Tr}_B(e^{\frac{i}{\hbar} H_B(t-\tau)} e^{-\frac{i}{\hbar} H_A(t-\tau)} e^{\frac{i}{\hbar} H_A t} e^{-\frac{i}{\hbar} H_B t} \sigma_B) \right] \tilde{\sigma}_{22}(t-\tau), \end{aligned} \quad (\text{B.5})$$

and

$$\frac{d\tilde{\sigma}_{22}}{dt} = - \frac{d\tilde{\sigma}_{11}}{dt}. \quad (\text{B.6})$$

Eq. (B.5) with a convoluted memory kernel for the rate constant is generally non-Markovian.

However, if the electronic coupling is weak one may use the Markovian approximation and the

nonadiabatic forward electron transfer rate k_{12} in the Markovian limit can be expressed by

$$k_{12} = \frac{U_{ax}^2}{\hbar^2 \text{Tr}_B(e^{-\beta H_b})} \int_{-\infty}^{\infty} d\tau \text{Tr}_B(e^{-\frac{i}{\hbar} H_b \tau} e^{(\frac{i}{\hbar} \tau - \beta) H_a}) . \quad (\text{B.7})$$

This formula is derived using only the property of the projection operator and, thus, it is valid for any general form of H_a and H_b .

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Figure Caption

Fig. 1. Schematic representation of two harmonic potential surfaces in one of the multi-dimensional reaction coordinate q_k . The potential profiles $U_{a,k}(q_k)$ for the reactant state and $U_{b,k}(q_k)$ the product state are assumed to have a different force constant with the bottom at $-x_{0,k}$ and $x_{0,k}$, respectively. E_g is the free-energy gap.

References

- [1] R. A. Marcus, J. Chem. Phys. 24 (1956) 966; 24 (1956) 979.
- [2] C. J. F. Böttcher, *Theory of Electric Polarization*, Vol. 1, (Elsevier Scientific Publishing, Amsterdam, 1973)
- [3] W. Jarzeba, K. Thakur and P.F. Barbara, Chem. Phys., (in press).
- [4] R.A. Marcus, J. Chem. Phys. 43 (1965) 679; P. Siders and R.A. Marcus, J. Am. Chem. Soc. 103 (1981) 741.
- [5] E. Buhks, M. Bixon, J. Jortner and G. Navon, J. Phys. Chem. 85 (1981) 3759; Inorg. Chem. 18 (1979) 2014.
- [6] T. Kakitani and N. Mataga, Chem. Phys. 93 (1985) 381.
- [7] T. Förster, Naturwiss. 33 (1946) 166; Ann. Physik, 2 (1948) 55; Z. Naturforsch. 417 (1949) 321.
- [8] D.L. Dexter, J. Chem. Phys. 21 (1953) 836.
- [9] T.F. Soules and C.B. Duke, Phys. Rev. B3 (1971) 262.
- [10] R.R. Dogonadze, A.M. Kuzentsov, Elektrokhimiya 3 (1967) 1324.
- [11] D. Rehm and A. Weller, Isr. J. Chem. 8 (1970) 259.
- [12] R. Englman and J. Jortner, Mol. Phys. 18 (1970) 145.
- [13] N.R. Kestner, J. Logan, J. Jortner, J. Phys. Chem. 78 (1974) 2148.
- [14] S. Efrima and M. Bixon, Chem. Phys. Lett. 25 (1974) 34.
- [15] J.J. Hopfield, Proc. Natl. Acad. Sci. U.S.A. 71 (1974) 3640.
- [16] J. Ulstrup and J. Jortner, J. Chem. Phys. 63 (1975) 4358.
- [17] J. Jortner, J. Chem. Phys. 64 (1976) 4860.

- [18] B.S. Brunschwig, J. Logan, M.D. Newton, N. Sutin, J. Am. Chem. Soc. 102 (1980) 5798.
- [19] A. Warshel and J-K. Hwang, J. Chem. Phys. 84 (1986) 4938.
- [20] J.S. Bader, R.A. Kuharski and D. Chandler, J. Chem. Phys. 93 (1990) 230.
- [21] J. Tang, J. Chem. Phys. 99 (1993) 5828.
- [22] A.J. Leggett, S. Chakravarty, A.T. Dorsey, M.P.A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. 59 (1985) 1.
- [23] A. Garg, J.N. Onnuchic, and V. Ambegaokar, J. Chem. Phys. 83 (1985) 4491.
- [24] J.N. Onnuchic, D.N. Beratan and J.J. Hopfield, J. Phys. Chem. 90 (1986) 3707.
- [25] I. Rips and J. Jortner, J. Chem. Phys. 87 (1987) 2090.
- [26] S. Chakravarty and A.J. Leggett, Phys. Rev. Lett. 52, 5 (1984).
- [27] J. Tang, J. Chem. Phys. 98, 6263 (1993); Chem. Phys. (in press).
- [28] L.D. Zusman, Chem. Phys. 49 (1980) 295.
- [29] G. van der Zwang and J.T. Hynes, J. Chem. Phys. 76 (1982) 2993; J. Phys. Chem. 89 (1985) 4181.
- [30] M. Sparpaglione and S. Mukamel, J. Chem. Phys. 88 (1988) 3263; Y.J. Yan, M. Sparpaglione and S. Mukamel, J. Phys. Chem. 92 (1988) 4842.
- [31] T. Fonseca, J. Chem. Phys. 91 (1989) 2869.
- [32] R.P. Feynman, *Statistical Mechanics*, (W.A. Bennjamin, Massachusetts, 1972).
- [33] S.H. Lin, J. Chem. Phys. 44 (1966) 3759.
- [34] R. Kubo and Y. Toyozawa, Prog. Theor. Phys. 13 (1955) 160.
- [35] P.G. Wolynes, J. Chem. Phys. 87 (1987) 6559.

[36] R.A. Kuharski, J.S. Bader, D. Chandler, M. Sprik, M.L. Klein and R.W. Impey, J. Chem. Phys. 89 (1988) 3248.

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