**The Generalized Spin-Boson Model for Electron-Transfer Reactions
Involving Two Harmonic Potentials
with a Different Force Constant**

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Abstract

The generalized spin-boson model is employed to analyze the electron-transfer reactions involving two harmonic potentials with a different force constant. An analytical expression for the nonadiabatic rate constant is derived with full consideration of the effects of quantum modes. For a single dominant solvent mode at low frequency, the result of the high temperature regime is reduced to the formula derived earlier based on the stochastic Liouville theory. For multiple soft solvent modes, the rate constant is a convoluted integral of a rate function for each individual single mode.

I. Introduction

Most theoretical treatments of electron-transfer reactions since the pioneering work of Marcus,¹ have assumed the same force constant for both Marcus free energy surfaces for the reactant and the 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 function² for the induced polarization is no longer a linear function of $\mu E/k_B T$. The problem for a system with two different force constants has been examined by Marcus³ and many others.^{4,5} Kakitani and Mataga⁴, for example, have applied the approach of Förster⁶ and Dexter⁷, 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 has been questioned earlier by Soules and Duke⁸ in their energy-transfer study, and it is invalid if a strong correlation exists between the interactions of the solvent bath with the reactant state and with the product state. In a recent study,⁵ we have employed 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. In this work, as an extension to our previous work which intrinsically assumes only an overdamped solvent motion, we use an alternative based on the generalized spin-boson model with full consideration of multiple quantum modes.

In the ordinary spin-boson model,⁸⁻¹⁵ one assumes a linear interaction between the fictitious spin representing the electronic states and the boson field representing the bath. Here

we will introduce a generalized spin-boson model by including an additional quadratic coupling between the "spin" and the bath. This Hamiltonian is equivalent to two sets of displaced harmonic oscillators with a different force constant in the multi-dimensional reaction coordinate. An analytical rate expression will be derived which include the tunnelling effects of high frequency quantum modes. In the high temperature limit, the rate expression can be reduced to our previous report⁵ using the stochastic Liouville theory for overdamped solvent motion.

II. The generalized spin-boson model

The ordinary spin-boson Hamiltonian⁸⁻¹⁵ 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

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

Here we use a fictitious spin-1/2 operator (S_α) to represent the two-level system of $|1\rangle$ and $|2\rangle$ which are eigenstates of S_z with eigenvalues $1/2$ and $-1/2$, respectively. The bath is assumed be consisted of an ensemble of harmonic oscillators. The last term describes the linear interaction between the fictitious spin representing the electronic states 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. (1) is equivalent to

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

One can gain a better physical picture with this expression than eq. (1). 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. (1) is related to the displacement $x_{0,k}$ by $C_k = 2m_k \omega_k^2 x_{0,k}$.

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

$$H = H_0 + H_I, \quad (3)$$

where H_0 is the Hamiltonian for the system and the bath, and H_I is for the electronic interaction between $|1\rangle$ and $|2\rangle$. They are given explicitly by

$$\begin{aligned} H_0 &= P H_a + (1-P) H_b \\ H_a &= \frac{1}{2} E_s + \sum_k \frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2 \\ H_b &= -\frac{1}{2} E_s + \sum_k \frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{b,k}^2 (q_k - x_{0,k})^2 \\ H_I &= 2U_{\alpha} S_x, \end{aligned} \quad (4)$$

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) and (4) can be reduced to eq. (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. (4) can be transformed into

$$H = E'_g S_z + 2U_{\alpha} S_x + \sum_k \left[\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 q_k^2 \right] + \sum_k C_k q_k S_z + \sum_k D_k q_k^2 S_z. \quad (5)$$

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

$$\begin{aligned} C_k &= m_k x_{0,k} \frac{4\omega_{a,k}^2 \omega_{b,k}^2}{\omega_{a,k}^2 + \omega_{b,k}^2} \\ D_k &= \frac{m_k}{2} (\omega_{a,k}^2 - \omega_{b,k}^2) \\ E'_g &= E_g - \sum_k \frac{m_k}{2} (\omega_{a,k}^2 - \omega_{b,k}^2) \left[\frac{2\omega_{a,k} \omega_{b,k}}{\omega_{a,k}^2 + \omega_{b,k}^2} \right]^2 x_{0,k}^2. \end{aligned} \quad (6)$$

The last term of the generalized spin-boson Hamiltonian in eq. (5) shows an additional quadratic coupling, proportional to q_k^2 , between the "spin" and the bath. In deriving the equivalence between the Hamiltonians defined in eqs. (4) and (5), we have again omitted a trivial constant energy term.

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

matrix by

$$\frac{\partial \tilde{\rho}}{\partial t} = \frac{i}{\hbar} [\tilde{\rho}, \tilde{H}_I(t)], \quad (7)$$

and

$$\tilde{H}_I(t) = e^{\frac{i}{\hbar} \hat{H}_B t} \hat{H}_I(t) e^{-\frac{i}{\hbar} \hat{H}_B t}. \quad (8)$$

To derive a rate equation involving only the electronic states $|1\rangle$ and $|2\rangle$, one can define a 2×2 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. (7) can be transformed into the following integrodifferential equation¹⁶

$$\frac{d\tilde{\sigma}}{dt} = - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \{ [\tilde{H}_I(t), [\tilde{H}_I(t-\tau), \sigma_B \tilde{\sigma}(t-\tau)]] \}, \quad (9)$$

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

$$\tilde{H}_I(t) = U_{\alpha\alpha} \begin{pmatrix} 0 & e^{\frac{i}{\hbar} H_{B1} t} e^{-\frac{i}{\hbar} H_{B2} t} \\ e^{\frac{i}{\hbar} H_{B2} t} e^{-\frac{i}{\hbar} H_{B1} t} & 0 \end{pmatrix}. \quad (10)$$

By substitution of eq. (10) into eq. (9), one can derive the following kinetic equation for the

populations $\tilde{\sigma}_{11}$ and $\tilde{\sigma}_{22}$

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

and

$$\frac{d\tilde{\sigma}_{22}}{dt} = - \frac{d\tilde{\sigma}_{11}}{dt} , \quad (12)$$

Eq. (11) 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

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2 \text{Tr}_B(e^{-\beta H_b})} \int_{-\infty}^{\infty} d\tau \text{Tr}_B(e^{-\frac{i}{\hbar}H_b\tau} e^{\frac{i}{\hbar}(\tau-\beta)H_a}) . \quad (13)$$

This formula is derived using only the property of the projection operator without assuming a specific form of H_a and H_b . Thus, it is valid for any other form of potential, although only the simple displaced harmonic potential is discussed here.

III. Analytical rate expressions for quantum modes

The Hamiltonians H_a and H_b in eq. (13) 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-known¹⁷ and it is given by

$$\begin{aligned}
 \langle x | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} | x' \rangle &= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \exp\left\{-\frac{m\omega}{2\hbar\sinh(\beta\hbar\omega)} [(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx']\right\} \\
 &= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \exp\left\{-\frac{m\omega}{4\hbar} [(x+x')^2 \tanh(\frac{\beta\hbar\omega}{2}) + (x-x')^2 \coth(\frac{\beta\hbar\omega}{2})]\right\}.
 \end{aligned} \tag{14}$$

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

$$\begin{aligned}
 \langle x | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2(q+x_0)^2)} | x' \rangle &= \langle x | e^{\frac{i}{\hbar}px_0} e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} e^{-\frac{i}{\hbar}px_0} | x' \rangle \\
 &= \langle x+x_0 | e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} | x'+x_0 \rangle.
 \end{aligned} \tag{15}$$

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. (4)

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

$$\begin{aligned}
 G_{a,k}(x_k, x'_k; \beta_1) &= \langle x_k | e^{-\beta_1 [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2]} | x'_k \rangle = \sqrt{\frac{m_k \omega_{a,k}}{2\pi \hbar \sinh(\beta_1 \hbar \omega_{a,k})}} \\
 &\quad \exp\left\{-\frac{m_k \omega_{a,k}}{4\hbar} \left[(x_k + x'_k + 2x_{0,k})^2 \tanh\left(\frac{\beta_1 \hbar \omega_{a,k}}{2}\right) + (x_k - x'_k)^2 \coth\left(\frac{\beta_1 \hbar \omega_{a,k}}{2}\right)\right]\right\} \\
 G_{b,k}(x_k, x'_k; \beta_2) &= \langle x_k | e^{-\beta_2 [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{b,k}^2 (q_k - x_{0,k})^2]} | x'_k \rangle = \sqrt{\frac{m_k \omega_{b,k}}{2\pi \hbar \sinh(\beta_2 \hbar \omega_{b,k})}} \\
 &\quad \exp\left\{-\frac{m_k \omega_{b,k}}{4\hbar} \left[(x_k + x'_k - 2x_{0,k})^2 \tanh\left(\frac{\beta_2 \hbar \omega_{b,k}}{2}\right) + (x_k - x'_k)^2 \coth\left(\frac{\beta_2 \hbar \omega_{b,k}}{2}\right)\right]\right\}.
 \end{aligned} \tag{16}$$

One can show from eqs. (13) and (16) that

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \prod_k \frac{\int_{-\infty}^{\infty} dx_k \int_{-\infty}^{\infty} dx'_k G_{b,k}(x_k, x'_k; \frac{i}{\hbar}\tau) G_{a,k}(x'_k, x_k; \beta - \frac{i}{\hbar}\tau)}{\int_{-\infty}^{\infty} dx_k G_{a,k}(x_k, x_k; \beta)}. \tag{17}$$

The double integrals over x and x' can be transformed into integrals over the new axes with $(x+x')/\sqrt{2}$ and $(x-x')/\sqrt{2}$ which can be carried out independently. The integration involving a gaussian is elementary and can be carried out easily. Eq. (17) can be reduced to

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \prod_k \exp \left[- \frac{4m_k \omega_{a,k} \omega_{b,k} x_{0,k}^2 / \hbar}{\omega_{a,k} \coth(\frac{\beta_2 \hbar \omega_{b,k}}{2}) + \omega_{b,k} \coth(\frac{\beta_1 \hbar \omega_{a,k}}{2})} \right] \sqrt{\frac{4\omega_{a,k} \omega_{b,k} \sinh^2(\frac{\beta \hbar \omega_{a,k}}{2})}{(\omega_{a,k}^2 + \omega_{b,k}^2) \sinh(\beta_1 \hbar \omega_{a,k}) \sinh(\beta_2 \hbar \omega_{b,k}) + 2\omega_{a,k} \omega_{b,k} [\cosh(\beta_1 \hbar \omega_{a,k}) \cosh(\beta_2 \hbar \omega_{b,k}) - 1]}} \quad (18)$$

where $\Omega = E_r/\hbar$, $\beta_1 = \beta - i\tau/\hbar$, and $\beta_2 = i\tau/\hbar$. A similar expression has also been obtained by Lin two decades ago in a different study of radiationless transitions.¹⁸ For the special case of equal force constants, i.e., $\omega_{a,k} = \omega_{b,k} = \omega_k$, eq. (18) can be reduced to a much simpler expression

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \exp \left\{ - \sum_k \frac{2m_k \omega_k x_0^2}{\hbar} \left[\coth\left(\frac{\beta \hbar \omega_k}{2}\right) (1 - \cos \omega_k \tau) + i \sin \omega_k \tau \right] \right\} . \quad (19)$$

This particular formula has been widely used in the analysis of electron or energy transfer processes due to quantum modes.^{8,14,15,19-24} One may use the steepest descent method^{3,25-27} to evaluate eq. (18) which can be expressed as

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

$$\Phi(\tau) = -iQ\tau + \sum_k \left[\frac{4m_k \omega_{a,k} \omega_{b,k} x_{0,k}^2 / \hbar}{\omega_{a,k} \coth(\frac{\beta_2 \hbar \omega_{b,k}}{2}) + \omega_{b,k} \coth(\frac{\beta_1 \hbar \omega_{a,k}}{2})} - \frac{1}{2} \ln[4\omega_{a,k} \omega_{b,k} \sinh^2(\frac{\beta \hbar \omega_{a,k}}{2})] \right. \quad (20)$$

$$\left. + \frac{1}{2} \ln[(\omega_{a,k}^2 + \omega_{b,k}^2) \sinh(\beta_1 \hbar \omega_{a,k}) \sinh(\beta_2 \hbar \omega_{b,k}) + 2\omega_{a,k} \omega_{b,k} [\cosh(\beta_1 \hbar \omega_{a,k}) \cosh(\beta_2 \hbar \omega_{b,k}) - 1]] \right] .$$

By expanding $\phi(\tau)$ around the saddle point τ_s where the first derivative $\phi'(\tau_s)$ vanishes, i.e.,

$\phi(\tau) = \phi(\tau_s) + \frac{1}{2} \phi''(\tau_s) (\tau - \tau_s)^2$, the rate expression can then be approximated by

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \sum_s \sqrt{\frac{2\pi}{\phi''(\tau_s)}} e^{-\Phi(\tau_s)} , \quad (21)$$

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.

IV. The High temperature regime

The rate expression in eq. (20) is complicate but very general. For an arbitrary spectral distribution of $\omega_{a,k}$ and $\omega_{b,k}$, one may use a numerical approach to carry out the time integral. However, we shall show that a simple relation can be derived if the spectral density is concentrated at very low frequency and the high temperature approximation holds. One may use the steepest descent method prescribed in eq. (21) or use the following approach which we prefer because it offers better physical insight into the connection to the stochastic Liouville theory used in our previous work.⁵ In this high temperature limit, the harmonic oscillators behave as

classical objects and their Hamiltonians H_a and H_b are assumed to be commutable. One has

$$\begin{aligned}
 & \langle x_k | e^{-\frac{i\tau}{\hbar} [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k - x_{0,k})^2]} e^{(i\frac{\tau}{\hbar} - \beta) [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2]} | x_k \rangle \\
 &= \langle x_k | e^{-\frac{i\tau}{\hbar} [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k - x_{0,k})^2]} + (i\frac{\tau}{\hbar} - \beta) [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2]} | x_k \rangle \\
 &= e^{\frac{i\tau}{\hbar} [\frac{1}{2} m_k \omega_{a,k}^2 (x_k + x_{0,k})^2 - \frac{1}{2} m_k \omega_{a,k}^2 (x_k - x_{0,k})^2]} \langle x_k | e^{-\beta [\frac{p_k^2}{2m_k} + \frac{1}{2} m_k \omega_{a,k}^2 (q_k + x_{0,k})^2]} | x_k \rangle \\
 &= \sqrt{\frac{m_k}{2\pi\beta\hbar^2}} e^{-\left(\beta - i\frac{\tau}{\hbar}\right) \frac{m_k \omega_{a,k}^2}{2} (x_k + x_{0,k})^2 - i\frac{\tau}{\hbar} \frac{m_k \omega_{b,k}^2}{2} (x_k - x_{0,k})^2} .
 \end{aligned} \tag{22}$$

Using eqs. (4) and (22), one can reduce eq. (13) to

$$\begin{aligned}
 k_{12} &= \frac{U_{ex}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} \prod_k \int_{-\infty}^{\infty} dx_k \sqrt{\frac{\beta m_k \omega_{a,k}^2}{2\pi}} \\
 &\cdot \exp\left\{ - \sum_k \frac{m_k \omega_{a,k}^2}{2} (\beta - i\frac{\tau}{\hbar}) (x_k + x_{0,k})^2 - i\frac{\tau}{\hbar} \sum_k \frac{m_k \omega_{b,k}^2}{2} (x_k - x_{0,k})^2 \right\} .
 \end{aligned} \tag{23}$$

Eq. (23) is an approximated form of eq. (18) in the high temperature regime.

Evaluation of the integrals over τ and x_k in eq. (23) 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. One has

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} dx \sqrt{\frac{\beta m \omega_s^2}{2\pi}} e^{-\frac{\beta m \omega_s^2}{2}(x+x_0)^2} \cdot 8\pi\hbar \delta[(E_{r,a}-E_{r,b})\frac{x^2}{x_0^2} + 2(E_{r,a}+E_{r,b})\frac{x}{x_0} + 4E_g + E_{r,a} - E_{r,b}] , \quad (24)$$

where we have defined two kinds of reorganization energy as

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

$$E_{r,b} = \frac{1}{2}m\omega_b^2(2x_0)^2 . \quad (25)$$

The δ -function in eq. (24) can be reduced to

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

$$= \frac{x_0}{4\sqrt{E_{r,a}E_{r,b}+E_g(E_{r,b}-E_{r,a})}} [\delta(x-x_{c1}) + \delta(x-x_{c2})] , \quad (26)$$

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

$$\begin{aligned}
x_{c1} &= x_0 \frac{(E_{r,a} + E_{r,b}) - 2 \sqrt{E_{r,a} E_{r,b} + E_s(E_{r,b} - E_{r,a})}}{E_{r,b} - E_{r,a}} \\
x_{c2} &= x_0 \frac{(E_{r,a} + E_{r,b}) + 2 \sqrt{E_{r,a} E_{r,b} + E_s(E_{r,b} - E_{r,a})}}{E_{r,b} - E_{r,a}} .
\end{aligned} \tag{27}$$

The integral in eq. (24) involving a δ -function is simple. With the help of eq. (26), one can obtain the following formula

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar} U_\alpha^2 \frac{1}{\sqrt{4\pi E_{r,b} k_B T (1 + \frac{E_s}{E_{r,a}} - \frac{E_s}{E_{r,b}})}} \exp\left\{-\frac{E_{r,a}(E_{r,b} - E_s)^2}{k_B T [E_{r,b} + \sqrt{E_{r,a} E_{r,b} + E_s(E_{r,b} - E_{r,a})}]^2}\right\} \\
&+ \frac{2\pi}{\hbar} U_\alpha^2 \frac{1}{\sqrt{4\pi E_{r,b} k_B T (1 + \frac{E_s}{E_{r,a}} - \frac{E_s}{E_{r,b}})}} \exp\left\{-\frac{E_{r,a}(E_{r,b} - E_s)^2}{k_B T [E_{r,b} - \sqrt{E_{r,a} E_{r,b} + E_s(E_{r,b} - E_{r,a})}]^2}\right\} .
\end{aligned} \tag{28}$$

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

Now we will discuss the case with multiple soft solvent modes. For many discrete low frequency solvent modes, eq. (23) can be expressed as

$$k_{12} = \frac{U_{\alpha}^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \prod_{k=1}^N \int_{-\infty}^{\infty} dx_k g_k(\tau, x_k) \quad (29)$$

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

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

$$\begin{aligned} & \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \prod_{k=1}^N g_k(\tau, x_k) \\ &= 2\pi\hbar \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \left(\frac{1}{2\pi\hbar}\right)^N \tilde{g}_1(E_1, x_1) \dots \tilde{g}_N(E_N, x_N) \delta(E_s - E_1 \dots - E_N) \end{aligned} \quad (30)$$

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

Using eq. (30) one can reduce eq. (29) to

$$\begin{aligned} k_{12} &= \frac{2\pi}{\hbar} U_{\alpha}^2 \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \delta(E_s - E_1 \dots - E_N) \\ &\quad \cdot \int_{-\infty}^{\infty} dx_1 \frac{\tilde{g}_1(E_1, x_1)}{2\pi\hbar} \dots \int_{-\infty}^{\infty} dx_N \frac{\tilde{g}_N(E_N, x_N)}{2\pi\hbar} \end{aligned} \quad (31)$$

The integral over x_k is very similar to the procedure as in the derivation of eq. (28). One can show

$$k_{12} = \frac{2\pi}{\hbar} U_{\alpha}^2 \int_{-\infty}^{\infty} dE_1 \dots \int_{-\infty}^{\infty} dE_N \delta(E_s - E_1 \dots - E_N) \hat{g}_1(E_1) \dots \hat{g}_N(E_N) \quad (32)$$

and

$$\begin{aligned} \hat{g}_k(E_k) &= \int_{-\infty}^{\infty} dx_k \frac{\hat{g}_k(E_k, x_k)}{2\pi\hbar} \\ &= \frac{1}{\sqrt{4\pi E_{r,k} k_B T (1 + \frac{E_k}{E_{r,k}} - \frac{E_k}{E_{r,b,k}})}} \exp\left\{ - \frac{E_{r,b,k} (E_{r,b,k} - E_k)^2}{k_B T [E_{r,b,k} + \sqrt{E_{r,s,k} E_{r,b,k} + E(E_{r,b,k} - E_{r,s,k})}]^2} \right\} \\ &\quad + \frac{1}{\sqrt{4\pi E_{r,b,k} k_B T (1 + \frac{E_k}{E_{r,s,k}} - \frac{E_k}{E_{r,b,k}})}} \exp\left\{ - \frac{E_{r,s,k} (E_{r,s,k} - E_k)^2}{k_B T [E_{r,s,k} - \sqrt{E_{r,s,k} E_{r,b,k} + E(E_{r,b,k} - E_{r,s,k})}]^2} \right\}, \end{aligned} \quad (33)$$

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

$$\begin{aligned} E_{r,s,k} &= \frac{1}{2} m_k \omega_{s,k}^2 (2x_{0,k})^2 \\ E_{r,b,k} &= \frac{1}{2} m_k \omega_{b,k}^2 (2x_{0,k})^2. \end{aligned} \quad (34)$$

The final rate expression in eq. (32) is more general which considers a multi-dimensional reaction coordinate whereas in the stochastic Liouville approach reported earlier only one-dimensional reaction coordinate is assumed.

V. Conclusions

We have applied a generalized spin-boson model with a quadratic coupling between the "spin" and the bath in this study of electron-transfer reactions involving quantum modes. 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. (20) an analytical formula for nonadiabatic electron-transfer rate. This general expression of the rate constant has considered the tunnelling 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 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. (28) 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 our previous work⁵ using an alternate one-dimensional stochastic Liouville theory for overdamped solvent motion. For multiple discrete modes at low frequency, the rate constant can be expressed in eq. (32) as a convolution of these quasi-gaussian functions for each individual mode. The convoluted integral can be simplified only if eq.(33) has a pure gaussian form which exists for the classical Marcus theory for two parabolas with an identical force constant.

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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 $U_{r,k}(q_k)$ for the reactant state and $U_{p,k}(q_k)$ 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.

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