Generalized Moment Expansion for Nonadiabatic Transition Reaction

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We discuss the generalized moments of the nonadiabatic transition reaction by using the stochastic Liouville equation for the study of outer-sphere electron transfer in polar solvents characterized by Debye dielectric relaxation. We obtain an approximate expression for the generalized moments which incorporates the width of the transition with arbitrary initial condition far from equilibrium. For low barriers, we derive an analytical expression for the rate corresponding to harmonic potential surfaces in the overdamped regime. For Fokker–Planck operators of Smoluchowski type, we introduce a new method to solve all of the generalized moments by using the eigenfunction expansion method.

1. INTRODUCTION

Since the pioneering work of Marcus and Hush,[1] electron transfer (ET) reactions have attracted a lot of attention. Solvent dynamic effects on the rate of electron transfer reaction have been the focus of experimental[2] and theoretical investigations. When the microscopic electronic processes are faster than the medium dielectric relaxation, the observed ET rate is determined by the longitudinal dielectric relaxation time τ_L. This solvent-controlled ET has been demonstrated by Kosower, Huppert, and co-workers.[2] The theory of solvent-controlled ET was first studied by Zusman,[3] using the stochastic Liouville equation method. Subsequently the solvent-controlled ET has been developed by using the generalized Langevin equation,[4] the mean-first-passage-time approach,[5] and path integral method.[6] Most of them are based on the assumption of a high

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barrier and thermal equilibrium initial condition. The ET rate assumes an Arrhenius form $k_{ET} = A \exp(-E_a/kT)$, where E_a is the activation energy. The preexponential frequency factor A is determined by the electronic coupling constant, the reorganization energy, the driving force, and τ_L. This implies the ET rate has a different time scale from a medium dielectric relaxation and can be described in terms of single-exponential decay. However, some chemical processes have little or no intrinsic barrier, e.g., some isomerization reactions, ET, and the primary charge separation step in photosynthesis.[7] The dynamics of activationless transition reactions differ considerably from those of high barrier conditions. Without the high barrier, the time scale of transition cannot be separated. The steady-state flux across the transition region cannot be obtained. The general time-independent rate constant is not valid. This implies that multiexponential decay relaxation processes may occur. The lowest nonzero eigenvalue of the kinetic equation may not be sufficient to describe the reaction, because the eigenvalue spectrum may be dense. Since the activationless transition is fast, the relaxation processes may depend on the initial condition. To explore the activationless and low-barrier transition reaction, short-time and long-time rates should be considered.

The solvent-controlled reaction rate obtained by Zusman in the normal regime, for sufficiently high barrier, is given by

$$k_{ET} = k_{NA}/\{1 + \kappa_A/[1 - (\Delta E/E_r)^2]\}$$

where k_{NA} is the nonadiabatic rate constant,

$$k_{NA} = [2\pi V_{12}^2/\hbar(4\pi E_r kT)^{1/2}] \exp(-E_A/kT)$$

while κ_A is the adiabaticity parameter

$$\kappa_A = 4\pi V_{12}^2 \tau_L/\hbar E_r$$

ΔE is the driving force (i.e., free energy gap), V_{12} is the electronic coupling constant, and E_r is the reorganization energy. The result is valid for the localized transition in both the normal and inverted regimes, but cannot be utilized for the activationless regime.

Less attention has been paid to activationless and low-barrier transition. Sumi and Marcus[5] and Zhu and Rasaiah[8] studied the Brownian motion on the harmonic potential surfaces with a Gaussian transition kernel and a thermal equilibrium initial condition. Rips and Jortner[9] studied the long-time transition rate for a localized transition. In our previous work[10] Zusman's equation has been extended to include delocalized transitions. Our results showed the validity in the inverted regime with the delocalization width up to the average length of the potential well. In

this paper we apply the Zusman stochastic Liouville equation to derive the generalized moments for short-time and long-time solvent-controlled rates of nonadiabatic transition reactions to include the low-barrier regime. In Section 2 we obtain a reduced Zusman equation which includes a delocalized transition. The generalized moments expansion of the probability density is defined. A projection operator method is applied to obtain the high-frequency moments with arbitrary initial conditions far from equilibrium. Application to the activationless case is also analyzed. To get the exact results of these moments, the four coupled equations for the diagonal and off-diagonal density matrix elements must be included. We introduce an eigenfunction expansion method in Section 3; the four coupled equations are expanded in a basis set of eigenfunctions of the Fokker–Planck operator for dynamics on averaged harmonic potential surfaces. The resulting matrix for the evolution of the density matrix expansion coefficients is a block tridiagonal matrix. The blocks are a 4×4 matrix corresponding to the four elements of the density matrix. An efficient way of solving the probability density fluctuation is based on a careful analysis of these tridiagonal equations with the probability conservation argument. The article is concluded in Section 4 with numerical results.

2. THE METHOD

2.1. Zusman Equation

Let us consider the transition between two shifted potential surfaces V_{11} and V_{22} which correspond to the donor and acceptor states, respectively. The transition between the diabatic potential surfaces is induced by the electronic coupling constant V_{12} (see Fig. 1). In condensed phases, these potential surfaces are coupled to a heat bath. The time evolution of this system obeys the Zusman equation (for a detailed derivation see ref. 10) for the coarse-grained density matrix ρ_{ij} $(i, j = 1, 2)$

$$\frac{\partial}{\partial t} \rho_{11} = L_{11} \rho_{11} - i \frac{V_{12}}{\hbar} (\rho_{21} - \rho_{12})$$

$$\frac{\partial}{\partial t} \rho_{22} = L_{22} \rho_{22} - i \frac{V_{12}}{\hbar} (\rho_{12} - \rho_{21})$$

$$\frac{\partial}{\partial t} \rho_{12} = L_{12} \rho_{12} - i \frac{V_{11} - V_{22}}{\hbar} \rho_{12} - i \frac{V_{12}}{\hbar} (\rho_{22} - \rho_{11})$$

$$\frac{\partial}{\partial t} \rho_{21} = L_{21} \rho_{21} - i \frac{V_{11} - V_{22}}{\hbar} \rho_{21} - i \frac{V_{12}}{\hbar} (\rho_{11} - \rho_{22})$$
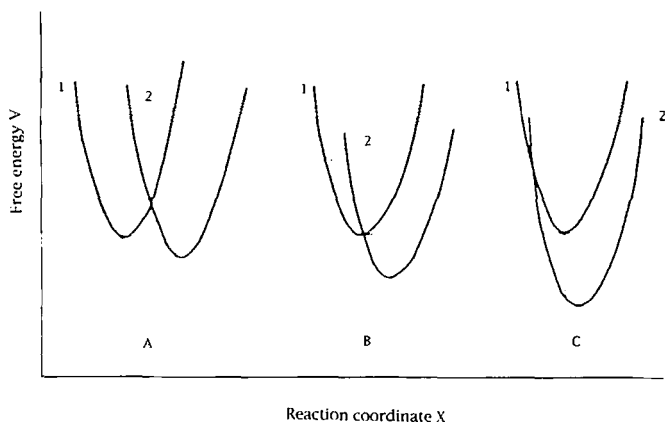
(1)

Fig. 1. Schematic illustration of the reactant (well 1) and product (well 2) potential energy surfaces for the nonadiabatic electron transfer reaction in the text: (A) normal regime; (B) activationless regime; (C) inverted regime. Notation: $a = 4\tau_L V_{12}/\hbar$, $\lambda = \omega_L \tau_L$, $\beta = 1/k_B T$, $S = \frac{1}{2} x_0^2 / \hbar \omega_L$, and $P = -\Delta E / \hbar \omega_L$.

where $\hbar$ is Planck's constant and L_{ij} is the Fokker–Planck operator. Here L_{ij} corresponds to the diffusion on surface i, and $L_{12} = \frac{1}{2}(L_{11} + L_{22})$ corresponds to the diffusion on the averaged potential surfaces $\frac{1}{2}(V_{11} + V_{22})$. These semiclassical equations describe the solvent dielectric fluctuation as a low-frequency fluctuation with energy smaller than $k_B T$. The diagonal elements ρ_{11} and ρ_{22} are the probabilities of finding the system in the initial and final potential wells. The diffusion motion is slow, since it is activated by thermal energy. The off-diagonal terms include not only the diffusion motion, but the high-frequency quantum transition behavior [$i(V_{22} - V_{11})/\hbar$ term]. Equation (1) can be reduced to two coupled equations by invoking the assumption that the off-diagonal element ρ_{12} varies with reaction coordinate much faster than the diagonal elements ρ_{11} and ρ_{22}. The reduced Zusman equation is

$$\frac{\partial}{\partial t} \rho = [L - K] \rho \tag{2}$$

with

$$\rho = [\rho_{11}, \rho_{22}]^T$$

$$L = \begin{bmatrix} L_{11} & 0 \\ 0 & L_{22} \end{bmatrix}$$

$$K(x) = 2 \operatorname{Re} K_{12}(x) \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

and

$$K_{12}(x) = \left(\frac{V_{12}}{\hbar}\right)^2 \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} d\tau \, G_{12}(x_1, \tau \mid x, 0)$$

where $G_{12}(x_1, \tau \mid x, 0)$ is the propagator $[\partial/\partial t - L_{12} + i(V_{22} - V_{11})/\hbar]^{-1}$. The G_{12} propagator describes motion in the well $\frac{1}{2}(V_{11} + V_{22})$ and quantum transition between V_{11} and V_{22}. $K(x)$ depends on the reaction coordinate and includes the information of delocalized transition. For a closed system, the forward k^{12} and backward k^{21} rate constants are defined from the population equations,

$$\frac{\partial}{\partial t}\begin{bmatrix} N_A \\ N_B \end{bmatrix} = \begin{bmatrix} -k^{12} & k^{21} \\ k^{12} & -k^{21} \end{bmatrix}\begin{bmatrix} N_A \\ N_B \end{bmatrix}$$

$$= -K\begin{bmatrix} N_A \\ N_B \end{bmatrix} \tag{3}$$

with

$$N_A = \int_{-\infty}^{\infty} dx \, \rho_{11}(x, t), \qquad N_B = \int_{-\infty}^{\infty} dx \, \rho_{22}(x, t)$$

the populations of states A and B, and $N_A + N_B = 1$. By using projection operator techniques on Eq. (2), we obtain an expression for the recrossing long-time transition rates

$$k^{12} = \frac{k_{NA}^{12}}{1 + k_{NA}^{12}/k_{D1} + k_{NA}^{21}/k_{D2}} \tag{4a}$$

$$k^{21} = \frac{k_{NA}^{21}}{1 + k_{NA}^{12}/k_{D1} + k_{NA}^{21}/k_{D2}} \tag{4b}$$

where

$$k_{NA}^{ij} = \int_{-\infty}^{\infty} dx \, \text{Re} \, K_{ij}(x) \, g_i(x) \tag{5a}$$

$$k_{Di}^{-1} = \int_0^{\infty} dt \, [G_{ii}^0(x^* \mid x^*, t) \, g_i^{-1}(x^*) - 1] \tag{5b}$$

Here $\text{Re} \, K_{12}(x)$ is the real part of the time integration of G_{12} and x^* is the crossing point. $g_i(x)$ is the equilibrium distribution in well i. k_{NA}^{ij} describes the motion along the surface as modulated by the surface splitting and a

delocalized transition. The rate k_{Di} characterizes the stochastic motion on the ith well. It also accounts for the deviation from equilibrium in the well that may occur if the crossing motion, characterized by k_{NA}^{ij}, is sufficiently fast.

2.2. Generalized Moment Expansion

Define the populations as the integration of probability density over space:

$$Q(t) = \int_{-\infty}^{\infty} dx \begin{bmatrix} \rho_{11}(x, t) \\ \rho_{22}(x, t) \end{bmatrix} = \begin{bmatrix} Q_1(t) \\ Q_2(t) \end{bmatrix} \tag{6}$$

with the probability conservation $Q_1(t) + Q_2(t) = 1$. Since our system is a closed system, the equilibrium distribution (i.e., the background)

$$Q^e = \int_{-\infty}^{\infty} dx \begin{bmatrix} \rho_{11}(x, t = \infty) \\ \rho_{22}(x, t = \infty) \end{bmatrix} \tag{7}$$

has to be subtracted from the population $Q(t)$. Also, define the fluctuation of populations via

$$\delta Q = Q(t) - Q^e \tag{8}$$

then $\lim_{t \to \infty} \delta Q(t) = 0$ and Q^e is unknown here. In terms of the Laplace transform

$$\delta \tilde{Q}(s) = \int_0^{\infty} dt \, e^{-st} \, \delta Q(t) \tag{9}$$

Eq. (8) has the following asymptotic expansions for low and high frequencies:

$$\delta \tilde{Q}(s) = \int_0^{\infty} dt \left(1 - st + \frac{1}{2!} s^2 t^2 - \cdots \right) \delta Q(t)$$

$$= \int_0^{\infty} dt \, \delta Q(t) - s \int_0^{\infty} dt \, t \, \delta Q(t) + \frac{1}{2!} s^2 \int_0^{\infty} dt \, t^2 \, \delta Q(t) + \cdots$$

$$= \delta \tilde{Q}(s=0) + s \, \delta \tilde{Q}'(s=0) + \frac{1}{2!} s^2 \, \delta \tilde{Q}''(s=0) + \cdots$$

$$= \left(\tau_0 - s\tau_1 + \frac{1}{2!} s^2 \tau_2 - \cdots \right) \begin{bmatrix} 1 \\ -1 \end{bmatrix} \quad \text{for} \quad s \to 0 \tag{10}$$

and

$$\delta\tilde{Q}(s) = \int_0^\infty dt \, e^{-st} [Q(t) - Q^e]$$

$$= \int_0^\infty dt \, e^{-st} \int_{-\infty}^\infty dx \, [e^{-(L-K)t}\rho(x,0) - Q^e]$$

$$= s^{-1}[Q(0) - Q^e] - s^{-2} \int_{-\infty}^\infty dx \, (L-K) \rho(x,0)$$

$$+ s^{-3} \int_{-\infty}^\infty dx \, (L-K)^2 \rho(x,0) + \cdots$$

$$= s^{-1}\mu_0 - s^{-2}\mu_1 + s^{-3}\mu_2 - \cdots \qquad \text{for} \quad s \to \infty \qquad (11)$$

where the expansion coefficients, i.e., the generalized moments, are given by $\tau_0, \tau_1, \tau_2,...$ and $\mu_0, \mu_1,...$.

From the definition given in Eq. (10), the mean first passage time and the averaged survival time are

$$\int_0^\infty dt \, \delta Q(t) = \left[\tilde{Q}(s) - \frac{1}{s} Q^e \right]_{s=0} \qquad (12)$$

and

$$\int_0^\infty dt \, t \, \delta Q(t) = -\frac{\partial}{\partial s} \left[\tilde{Q}(s) - \frac{1}{s} Q^e \right]_{s=0} \qquad (13)$$

respectively. Applying the known initial conditions $\int_{-\infty}^\infty dx \, \rho_{11}(x, t=0) = 1$, $\rho_{22}(x, t=0) = \rho_{12}(x, t=0) = \rho_{21}(x, t=0) = 0$, and the boundary condition $\int_{-\infty}^\infty dx \, L(\cdot) = 0$ to Eq. (11), we obtain the moments corresponding to high frequency as

$$\mu_0 = Q(0) - Q^e \qquad (14a)$$

$$\mu_1 = \int_{-\infty}^\infty dx \, K\rho_{11}(x, 0) \qquad (14b)$$

$$\mu_2 = \int_{-\infty}^\infty dx \, K(L-K) \rho(x, 0) \qquad (14c)$$

$\cdots$

By using projection operator techniques on Eq. (2) and comparing with Eq. (11), we can obtain the moments corresponding to low frequency.

Define the projection operator $P = g \int dx$ and its complement $Q = 1 - P$, where g is a 2 by 2 diagonal matrix of equilibrium distribution at each well

$$g_i = e^{-\beta V_{ii}} \bigg/ \int_{-\infty}^{\infty} dx\, e^{-\beta V_{ii}}, \qquad i = 1, 2$$

Applying P and Q to the Laplace transform of Eq. (2), we find that standard projection operator manipulation leads to

$$\tilde{Q}(s) = g^{-1}\{s + PK + PK[s - Q(L - K)]^{-1}Q(L - K)\}^{-1}$$
$$\times \{P\rho(0) - PK[s - Q(L - K)]^{-1}Q\rho(0)\} \qquad (15)$$

The first term of Eq. (15) is analyzed with the use of the identity

$$(s - QL + QK)^{-1} = (s - QL)^{-1} - (s - QL)^{-1}QK(s - QL + QK)^{-1}$$

and the boundary condition $PL = 0$. Iterating this identity, we have

$$(s - QL + QK)^{-1} = \tilde{G}^0 - \tilde{G}^0 QK\tilde{G}^0 + \cdots \qquad (16)$$

with $\tilde{G}^0 = (s - QL)^{-1}$.

We solve Eq. (15) with the consecutive approximation (see ref. 10) in which the dynamics of diffusion and reaction are disentangled, i.e.,

$$g^{-1}\{s + PK + PK[s - Q(L - K)]^{-1}Q(L - K)\}^{-1}g$$
$$= [s(1 + g^{-1}\bar{\tilde{G}}^0 K^{eq}) + K^{eq}]^{-1}(1 + g^{-1}\bar{\tilde{G}}^0 K^{eq}) \qquad (17a)$$

and

$$g^{-1}PK[s - Q(L - K)]^{-1}Q\rho(0)$$
$$= K^{eq}(s + g^{-1}\bar{\tilde{G}}^0 K^{eq})^{-1} g^{-1}\tilde{G}^0 Q\rho(0) \qquad (17b)$$

Using the identity given in Eq. (16) and the approximation given in Eq. (17), we obtain the Laplace transform of population

$$\tilde{Q}(s) = (1 + g^{-1}\bar{\tilde{G}}^0 K^{eq})[s(1 + g^{-1}\bar{\tilde{G}}^0 K^{eq}) + K^{eq}]^{-1}$$
$$\times \left[\int dx\, \rho(0) + K^{eq}(1 + g^{-1}\bar{\tilde{G}}^0 K^{eq})^{-1} g^{-1}\tilde{G}^0 Q\rho(x, t = 0) \right] \qquad (18)$$

where

$$\int dx\, \rho(x, t = 0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad (19)$$

$$Q\rho(x, t = 0) = (-1)\begin{bmatrix} \rho_{11} - g_1 \\ 0 \end{bmatrix} \qquad (20)$$

$$K^{\mathrm{eq}} = \begin{bmatrix} k_{NA}^{12} & -k_{NA}^{21} \\ -k_{NA}^{12} & k_{NA}^{21} \end{bmatrix} \tag{21}$$

$$\bar{\tilde{G}}^0 = \tilde{G}^0(x^*; x^*, s) - \int dy\, \tilde{G}^0(x^*; x^*, s)\, g(y) \tag{22}$$

Finally, the contribution of Eq. (18) gives

$$\begin{aligned}
\tilde{Q}_2(s) &= \frac{1}{s} - \tilde{Q}_1(s) \\
&= [s^2(1 + g_1^{-1}\bar{\tilde{G}}_{11}^0 k_{NA}^{12} + g_2^{-1}\bar{\tilde{G}}_{22}^0 k_{NA}^{21}) + s(k_{NA}^{12} + k_{NA}^{21})]^{-1} \\
&\quad \times k_{NA}^{12}[1 - sg_1^{-1}\tilde{G}_{11}^0(\rho_{11} - g_1)]
\end{aligned} \tag{23}$$

In the long-time limit, $s \to 0$,

$$\begin{aligned}
\bar{\tilde{G}}_{ii}^0 &= \tilde{G}_{ii}^0(x^*, s; x^*) - \int dy\, \tilde{G}_{ii}^0(x^*, s; y, 0)\, g_i(y) \\
&= \int_0^\infty dt\, [G_{ii}^0 g_i^{-1} - 1] - s\int_0^\infty dt\, t[G_{ii}^0 g_i^{-1} - 1] \\
&\quad + \frac{1}{2!}s^2 \int_0^\infty dt\, t^2[G_{ii}^0 g_i^{-1} - 1] + \cdots \\
&= k_{Di}^{(0)^{-1}} - sk_{Di}^{(1)^{-1}} + \frac{1}{2!}s^2 k_{Di}^{(2)^{-1}} + \cdots
\end{aligned}$$

where we define the diffusion moments as

$$\int_0^\infty dt\, t^n[G_{ii}^0 g_i^{-1} - 1] = k_{Di}^{(n)^{-1}} \tag{24}$$

For the zeroth-order approximation,

$$g_i^{-1}\bar{\tilde{G}}_{ii}^0 \approx k_{Di}^{(0)^{-1}} \tag{25}$$

$$\tilde{Q}_2(s) = \frac{k^{12}}{s(s + k^{12} + k^{21})} \tag{26}$$

This is the result of a phenomenological first-order rate law with one relaxation time $1/(k^{12} + k^{21})$. Using the singularity analysis of $\tilde{Q}(s)$, we find the equilibrium distributions

$$Q_1^e = \frac{k^{21}}{k^{12} + k^{21}}, \qquad Q_2^e = \frac{k^{12}}{k^{12} + k^{21}} \tag{27}$$

and we obtain the fluctuation of populations

$$\delta\tilde{Q}_2(s) = \frac{k_{NA}^{12}[1 + sg_1^{-1}\tilde{G}_{11}^0(g_1 - \rho_{11})]}{s[k_{NA}^{12} + k_{NA}^{21} + s(1 + g_1^{-1}\tilde{G}_{11}^0 k_{NA}^{12} + g_2^{-1}\bar{\tilde{G}}_{22}^0 k_{NA}^{21})]} - \frac{k_{NA}^{12}}{k_{NA}^{12} + k_{NA}^{21}}\frac{1}{s}$$

and

$$\delta\tilde{Q}_1 = -\delta\tilde{Q}_2$$

Finally we have all of the moments, e.g.,

$$\tau_0 = Q_2^e(k_{0,D1}^{\text{ini}^{-1}} - \tau), \qquad \tau = (k^{12} + k^{21})^{-1} \tag{28}$$

$$\tau_1 = Q_2^e\left(-k_{1,D1}^{\text{ini}^{-1}} + Q_1^e k_{1,D2}^{-1} + Q_2^e k_{1,D1}^{-1} + \tau^2 - \frac{\tau}{k_{0,D1}^{\text{ini}}}\right) \tag{29}$$

where we have used the series expansion

$$g_1^{-1}\tilde{G}^0(\rho_{11} - g_1(x^*)) = \sum_{n=0}^{\infty} k_{n,D1}^{\text{ini}^{-1}}(-s)^n$$

The other higher moments can be obtained in the same way.

2.3. Relaxation Times

The first-order kinetics that we used in ref. 10 is based on the assumption that the reaction starts in a near equilibrium configuration and the equilibrium state is approximately maintained during the reaction. In the activationless regime, the rate is fast and the initial configuration is usually far from the equilibrium distribution. The reaction rate $(\partial/\partial t) Q_2(t)$ should vanish initially, approach some maximum rate at later time, and finally decay to zero. This needs a multiple-exponential decay time description. A polynomial expansion of $\delta\tilde{Q}_2(s)$ in terms of low frequency or high frequency cannot give us an accurate description, and the difficulty of using Mori's relaxation theory is due to the non-Hermitian form of the Fokker–Planck operator. We will study this problem in a future work. In this section we evaluate two relaxation times from the known information of the moments:

1. Probability conservation, i.e., $Q_1(t) + Q_2(t) = 1$.
2. $(\partial/\partial t) Q_2(t)|_{t=0} = 0$.

In our harmonic oscillator potential surface model, the initial conditions $\rho_{12} = \rho_{21} = 0$ imply this condition (see Section 4.3).

3. $\int_0^{\infty} dt\, \delta Q(t) = \tau_0$.
4. $\int_0^{\infty} dt\, \delta Q(t) = \tau_1$.

Assume a two-relaxation-time description of the population in well 2,

$$Q_2(t) = Q_2^e + ae^{-\lambda_1 t} + be^{-\lambda_2 t} \tag{30}$$

With the conditions 1–4, we obtain

$$a = -\frac{1/\lambda_1}{1/\lambda_1 - 1/\lambda_2} Q_2^e, \qquad b = \frac{1/\lambda_2}{1/\lambda_1 - 1/\lambda_2} Q_2^e$$

and

$$\frac{1}{\lambda_{1,2}} = \frac{1}{2}\frac{\tau_0}{Q_2^e} + \left(\frac{\tau_1}{Q_2^e} - \frac{3}{4}\frac{\tau_0^2}{(Q_2^e)^2}\right)^{1/2} \tag{31}$$

In the following section, the application of τ_0, τ_1 and λ_1, λ_2 to specific models will be discussed.

2.4. Application to Harmonic Potential Surfaces

In this section, we obtain an approximate rate constant expression given in Section 2.3 with a special model of harmonic potential surfaces. With a given initial distribution (delta function and Gaussian distribution function), we evaluate τ_0 and τ_1. The harmonic potential surfaces are given in Eq. (42). The stochastic processes correspond to overdamped Brownian motion, i.e.,

$$L_{ii} = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \beta\frac{\partial}{\partial x} V_{ii}\right), \qquad i = 1, 2$$

and

$$L_{12} = L_{21} = \tfrac{1}{2}(L_{11} + L_{22})$$

Here D is the diffusion coefficient and $\beta = 1/k_B T$.

The exact solution of the propagator of the off-diagonal term is[12]

$$\begin{aligned}
G_{21}(x, t \mid x_i, 0) = &\frac{1}{(2\pi D\tau_L)^{1/2}} \frac{1}{(1 - e^{-2t})^{1/2}} \exp\left(\frac{1}{2}\frac{1}{D\tau_L}\frac{1}{1 - e^{-2t}}\right. \\
&\times \left\{2D\frac{\gamma\tau_L^2}{\hbar}(1 - e^{-t}) - i\left[x - x_i e^{-t} - \frac{1}{2}x_0(1 - e^{-t})\right]\right\}^2 \\
&\left. - D\left(\frac{\gamma\tau_L}{\hbar}\right)^2 \tau_L t + i\frac{\gamma\tau_L}{\hbar}\left(x - x_i - \frac{1}{2}x_0 t + \sigma t\right)\right) \tag{32}
\end{aligned}$$

where σ is the crossing point and $\gamma = k_\omega x_0$ is the force difference at the crossing point. The use of Eq. (32) in Eq. (5a) yields the nonadiabatic transition rate

$$k_{NA}^{12} = 2\left(\frac{a}{4}\right)^2 \frac{1}{\tau_L^2} \int dt\,dx\,dx_i\,\mathrm{Re}\,G_{21}(x, t \mid x_i, 0)\,g_1(x_i)$$

$$= 2\left(\frac{a}{4}\right)^2 \frac{1}{\tau_L}\,\mathrm{Re}\int dt\,\exp\left(-2\left(\frac{\lambda}{\beta\hbar\omega_L}\right)^2 (-1+t+e^{-t})\right)$$

$$\times \left[(\beta\,\Delta G_1^\neq)^{1/2} + (\beta\,\Delta G_2^\neq)^{1/2}\right]^2$$

$$+ i\,\frac{\lambda}{\beta\hbar\omega_L}\left\{\left[(\beta\,\Delta G_1^\neq)^{1/2} + (\beta\,\Delta G_1^\neq)^{1/2}\right]^2 (-1+t+e^{-t})\right.$$

$$\left. - 2\left[\beta\,\Delta G_1^\neq + (\beta\,\Delta G_1^\neq \cdot \beta\,\Delta G_2^\neq)^{1/2}\right]t\right\}\Bigg)$$

$$= 2\left(\frac{a}{4}\right)^2 \frac{1}{\tau_L}\,\mathrm{Re}\,\exp\left\{\frac{\lambda}{\beta\hbar\omega_L}\left(\frac{2\lambda}{\beta\hbar\omega_L} - i\right)\right.$$

$$\times \left[2(\beta\,\Delta G_1^\neq)^{1/2} - (\beta E_r)^{1/2}\right]^2\Bigg\}\,B^{-\mu}\gamma(\mu, B) \qquad (33a)$$

where

$$B = \left(\frac{\lambda}{\beta\hbar\omega_L}\right)^2 2(x+y)^2 - i\,\frac{\lambda}{\beta\hbar\omega_L}\,(x+y)$$

$$\mu = \left(\frac{\lambda}{\beta\hbar\omega_L}\right)^2 2(x+y)^2 + i\,\frac{\lambda}{\beta\hbar\omega_L}\,(y-x)$$

$$x = \beta\,\Delta G_1^\neq, \qquad y = \beta\,\Delta G_1^\neq - 2(\beta\,\Delta G_1^\neq\,\beta E_r)^{1/2} + \beta E_r$$

$$\gamma(\mu, B) = \sum_{n=0}^{\infty} \frac{(-1)^n\,B^{n+\mu}}{n!\,(\mu+n)}$$

and

$$k_{NA}^{21} = 2\left(\frac{a}{4}\right)^2 \frac{1}{\tau_L^2} \int dt\,dx\,dx_i\,\mathrm{Re}\,G_{12}(x, t \mid x_i, 0)\,g_2(x_i)$$

$$= 2\left(\frac{a}{4}\right)^2 \frac{1}{\tau_L}\,\mathrm{Re}\int dt\,\exp\left(-2\left(\frac{\lambda}{\beta\hbar\omega_L}\right)^2 (-1+t+e^{-t})\right)$$

$$\times \left[(\beta\,\Delta G_1^\neq)^{1/2} + (\beta\,\Delta G_2^\neq)^{1/2}\right]^2$$

$$- i\,\frac{\lambda}{\beta\hbar\omega_L}\left\{\left[(\beta\,\Delta G_1^\neq)^{1/2} + (\beta\,\Delta G_1^\neq)^{1/2}\right]^2 (1+t-e^{-t})\right.$$

$$\left. - 2\left[\beta\,\Delta G_1^\neq + (\beta\,\Delta G_1^\neq \cdot \beta\,\Delta G_2^\neq)^{1/2}\right]t\right\}\Bigg)$$

$$= 2 \left(\frac{a}{4}\right)^2 \frac{1}{\tau_L} \operatorname{Re} \exp\left\{\frac{\lambda}{\beta\hbar\omega_L}\left(\frac{2\lambda}{\beta\hbar\omega_L} + i\right)\right.$$

$$\times \left. [2(\beta \, \Delta G_2^{\neq})^{1/2} + (\beta E_r)^{1/2}]^2\right\} B^{-\mu}\gamma(\mu, B) \tag{33b}$$

where

$$\mu = \left(\frac{\lambda}{\beta\hbar\omega_L}\right)^2 2(x+y)^2 - i\frac{\lambda}{\beta\hbar\omega_L}(y-x)$$

$$x = [(\beta \, \Delta G_2^{\neq})^{1/2} + (\beta E_r)^{1/2}]^2, \qquad y = \beta \, \Delta G_2^{\neq}$$

The diffusion rate constants on each well are

$$k_{D1}^{-1} = g_1^{-1}\bar{\bar{G}}_{11}^0$$

$$= \tau_L \int dt \, e^{-st}[G_{11}^0(x^*; x^*, t) \, g_1^{-1}(x^*) - 1]$$

$$= k_{0,D1}^{-1} - sk_{1,D1}^{-1} + \frac{1}{2!} s^2 k_{2,D1}^{-1} - \cdots$$

$$= \left[B\left(\frac{1}{2}, s\right)\Phi_1\left(\frac{1}{2}, s, s+\frac{1}{2}, -1, -\beta \, \Delta G_1^{\neq}\right)\exp(\beta \, \Delta G_1^{\neq}) - \frac{1}{s}\right]\tau_L \tag{34a}$$

where

$$B(x, y) = \frac{1}{y} \sum_{n=0}^{\infty} (-1)^n \frac{y(y-1)\cdots(y-n)}{n!\,(x+n)}, \qquad y > 0$$

$$= \text{beta function}$$

$$\Phi_1(\alpha, \beta, \gamma, x, y) = \sum_{m,n=0}^{\infty} \frac{(\alpha)_{m+n}(\beta)_n}{(\gamma)_{m+n}\,m!\,n!} x^m y^n, \qquad |x| < 1$$

$$= \text{degenerate hypergeometric series}$$

$$(\alpha)_0 = 1, \qquad (\alpha)_m = \alpha(\alpha+1)\cdots(\alpha+m-1)$$

and

$$k_{D2}^{-1} = g_2^{-1}\bar{\bar{G}}_{22}^0$$

$$= \tau_L \left[\exp(\beta \, \Delta G_2^{\neq}) \, B\left(\frac{1}{2}, s\right)\Phi_1\left(\frac{1}{2}, s, s+\frac{1}{2}, -1, -\beta \, \Delta G_2^{\neq}\right) - \frac{1}{s}\right] \tag{34b}$$

Introducing a series expansion of Eq. (34a), we find for the diffusion moments

$$k_{0,D1}^{-1} = g_1^{-1}(x^*)[-I(0) + S(\tfrac{1}{2}\beta \, \Delta G_1^{\neq})] \tag{35a}$$

$$k_{1,D1}^{-1} = g_1^{-1}(x^*) \sum_{n=0}^{\infty} \frac{1}{n!}(-\beta \, \Delta G_1^{\neq})^n J_1(n) \tag{35b}$$

where

$$I(n) = -\ln 2 + \sum_{m=1}^{n} \frac{1}{m - 1/2}$$

$$= 0.577215 + \ln 2 + \Psi\left(n + \frac{1}{2}\right)$$

$$\Psi(x) = \text{Euler's psi function}$$

$$S(x) = \sum_{n=1}^{\infty} (-1)^{n-1} I(n) \frac{x^n}{n!}$$

$$J_m(n) = m! \left\{ \sum_{k=1}^{\infty} \frac{1}{k!} \left[\left(n+\frac{1}{2}\right)_{-k} + \left(n+\frac{1}{2}\right)_{k-2} \right] (-1)^k k^{-m-1} \right.$$

$$\left. + \sum_{i,m=1}^{\infty} \frac{(n+1/2)_{-k} (n+1/2)_{n-2}}{k! \, i!} (-1)^{k+i} (k+i)^{-m-1} \right\}$$

$k_{0,D2}^{-1}$ and $k_{1,D2}^{-1}$ can be obtained from Eq. (35) by replacing $\beta \, \Delta G_1^{\neq}$ by $\beta \, \Delta G_2^{\neq}$.

When the initial distribution is a delta function, $\delta(y - y_0)$, the numerator of Eq. (23) is given by

$$g_1^{-1} \tilde{G}_{11}^0 (\rho - g) = g_1^{-1}(x^*) \int dy \, \tilde{G}_{11}^0 (x^*, s \mid y)[\delta(y - y_0) - g(y)]$$

$$= \sum_{n=0}^{\infty} \frac{(-s)^n}{n!} k_{n,D1}^{\text{ini}-1}$$

$$= \int dt \, e^{-st} \left\{ (1 - e^{-2t})^{-1/2} \exp\left[\frac{1}{2} \frac{(x^* - y_0 e^{-t})^2}{1 - e^{-2t}} \right] - 1 \right\} \tag{36a}$$

$$= 2^{s/2-1} \Gamma\left(\frac{s}{2}\right) \exp\left(-\frac{1}{4} y_0^2\right) D_{-s}(y_0) - \frac{1}{s} \quad \text{for} \quad x^* = 0 \tag{36b}$$

where Γ = gamma function, $D_p(z)$ = parabolic cylinder function.

For the Gaussian initial distribution function $(2\pi)^{-1/2} \exp[-\frac{1}{2}(y-y_0)^2]$ the numerator is

$$g_1^{-1}\tilde{G}_{11}^0(\rho_{11} - g_1) = \int dt\, e^{-st} \left\{ \exp\left[\frac{1}{2}x^{*2} - \frac{1}{2}(x^* - y_0 e^{-t})^2 \right] - 1 \right\} \quad (37a)$$

$$= \frac{1}{2}\left(\frac{1}{2}y_0^2 \right)^{-s/2} \gamma\left(\frac{s}{2}, \frac{1}{2}y_0^2 \right) - \frac{1}{s} \quad \text{for} \quad x^* = 0 \quad (37b)$$

where $\gamma(\alpha, x)$ = incomplete gamma function. The diffusion moments are

$$k_{0,D1}^{\text{ini}^{-1}} = \frac{1}{2}[\text{Ei}(-x) - \ln x], \qquad x = \frac{1}{2}y_0^2$$

where Ei = exponential integral function, and

$$k_{1,D1}^{\text{ini}^{-1}} = \frac{1}{4} \sum_{n=1}^{\infty} \frac{(-\frac{1}{2}y_0^2)^n}{n^2\, n!}$$

Equations (33)–(36) give all of the factors in Eqs. (28) and (29).

2.5. Limiting Case

The general expression from Eqs. (23) and (24) gives good numerical results compared to the exact numerical calculation in Section 3. In this section, we give some limiting expressions of k_{NA}^{ij} and k_{Di} in the overdamped regime.

The forward and backward nonadiabatic transition rates are given by

$$k_{NA}^{12} = \left(\frac{a}{4} \right)^2 \frac{1}{\tau_L} \frac{\beta\hbar\omega_L}{\lambda} \left(\frac{2\pi}{\beta E_r} \right)^{1/2} \exp\left[-\frac{1}{2}\beta E_r \left(1 - \frac{\beta \Delta E}{\beta E_r} \right)^2 \right] \quad (38a)$$

and

$$k_{NA}^{21} = \left(\frac{a}{4} \right)^2 \frac{1}{\tau_L} \frac{\beta\hbar\omega_L}{\lambda} \left(\frac{2\pi}{\beta E_r} \right)^{1/2} \exp\left[-\frac{1}{2}\beta E_r \left(1 + \frac{\beta \Delta E}{\beta E_r} \right)^2 \right] \quad (38b)$$

In the activationless regime, with $\beta \Delta G_1^{\neq} = 0$ and $\beta \Delta G_2^{\neq} \gg 1$, we have

$$k_{NA}^{12} = \left(\frac{a}{4} \right)^2 \frac{1}{\tau_L} \frac{\beta\hbar\omega_L}{\lambda} \left(\frac{\pi}{\beta \Delta G_2^{\neq}} \right)^{1/2} \quad (39)$$

and

$$k_{NA}^{21} = \left(\frac{a}{4} \right)^2 \frac{1}{\tau_L} \frac{\beta\hbar\omega_L}{\lambda} \left(\frac{\pi}{\beta \Delta G_2^{\neq}} \right)^{1/2} \exp(-\beta \Delta G_2^{\neq}) \quad (40)$$

The diffusion rate constant is given by

$$k_{D1}^{-1} = \tau_L \ln 2, \qquad\qquad\qquad\qquad \beta \, \Delta G_1^{\neq} = 0 \qquad (41a)$$

$$= \exp(\beta \, \Delta G_1^{\neq})[-I(0) + \beta \, \Delta G_1^{\neq} \, I(1)], \qquad \beta \, \Delta G_1^{\neq} \ll 1 \qquad (41b)$$

$$= \tau_L \left(\frac{\pi}{\beta \, \Delta G_1^{\neq}} \right)^{1/2} \exp(\beta \, \Delta G_1^{\neq}), \qquad \beta \, \Delta G_1^{\neq} \gg 1 \qquad (41c)$$

Note that the diffusion rate is a constant in the activationless regime and depends on $\beta \, \Delta G_1^{\neq}$ linearly in the low-barrier regime.

3. NUMERICAL METHOD

In this section, we calculate the generalized moments by solving the four coupled equations given in Eq. (1). We use the standard harmonic oscillator model as the potential surfaces

$$V_{11} = \tfrac{1}{2} m \omega^2 x^2 \qquad\qquad\qquad\qquad\qquad (42a)$$

$$V_{22} = \tfrac{1}{2} m \omega^2 (x - x_0)^2 + \Delta E \qquad\qquad\qquad (42b)$$

where ΔE is the driving force ($\Delta E < 0$ for an exothermic process, and $\Delta E > 0$ for an endothermic process) and x_0 is the horizontal displacement. The stochastic process corresponding to overdamped Brownian motion is the Smoluchowski operator

$$L_{ii} = D \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} + \beta \frac{\partial}{\partial x} V_{ii} \right), \qquad i = 1, 2$$

and

$$L_{12} = L_{21} = \tfrac{1}{2}(L_{11} + L_{22})$$

It is useful to transform the coupled equations into density matrix element combinations and to introduce a basis set expansion of the density matrix with basis function proportional to Hermite polynomials:

$$\rho^{\pm} = \rho_{11} \pm \rho_{22} = \sum_{n=0}^{\infty} a_n^{\pm}(t) \, r_n \left(\frac{y}{\sqrt{2}} \right) \qquad (43a)$$

$$\mathrm{Re} \, \rho_{12} = \frac{1}{2}(\rho_{12} + \rho_{12}) = \sum_{n=0}^{\infty} b_n^{+} r_n \left(\frac{y}{\sqrt{2}} \right) \qquad (43b)$$

$$\mathrm{Im} \, \rho_{12} = \frac{1}{2i}(\rho_{12} - \rho_{12}) = \sum_{n=0}^{\infty} b_n^{-} r_n \left(\frac{y}{\sqrt{2}} \right) \qquad (43c)$$

The argument y is equal to $x - \frac{1}{2}x_0$ and r_n is the right eigenfunction of the Fokker–Planck operator L_{12}, i.e.,

$$\left[\frac{\partial^2}{\partial x^2} + \left(x - \frac{1}{2}x_0\right)\frac{\partial}{\partial x} + 1\right] r_n = \mu_n r_n \tag{44}$$

where

$$r_n = (2^n n!)^{-1/2} (1/2\pi)^{1/4} e^{-y^2/2} H_n\left(\frac{y}{\sqrt{2}}\right) \tag{45}$$

and the eigenvalue $\mu_n = -n$, $n = 0, 1, 2,\ldots$. We define a dimensionless time $\bar{t} = D\beta m\omega^2 t = t/\tau_L$, where τ_L is the longitudinal dielectric relaxation time of the overdamped oscillator, and a dimensionless coordinate $\bar{x} = (m\omega^2\beta)^{1/2} x$, where $(m\omega^2\beta)^{-1/2}$ is the average width of the oscillator surfaces. It is useful to transform the Zusman equation to a set of first-order differential equations

$$\frac{\partial}{\partial t} a_n^+ = \mu_n a_n^+ - \frac{1}{2}x_0 \sqrt{n}\, a_{n-1}^- \tag{46a}$$

$$\frac{\partial}{\partial t} a_n^- = \mu_n a_n^- - \frac{1}{2}x_0 \sqrt{n}\, a_{n-1}^+ - ab_n^- \tag{46b}$$

$$\frac{\partial}{\partial t} b_n^+ = \mu_n b_n^+ + b \sqrt{n}\, b_{n-1}^- + b(n+1)^{1/2} b_{n+1}^- - b\sigma_y b_n^- \tag{46c}$$

$$\frac{\partial}{\partial t} b_n^- = \mu_n b_n^- - b \sqrt{n}\, b_{n-1}^+ - b(n+1)^{1/2} b_{n+1}^+ + b\sigma_y b_n^+ + \frac{1}{4} aa_n^- \tag{46d}$$

where

$$a = \frac{4V_{12}\tau_L}{\hbar}, \qquad b = \left(\frac{2E_r/\hbar\omega_L}{\beta\hbar\omega_L}\right)^{1/2}$$

E_r is the reorganization energy, and $\sigma_y = \sigma - \frac{1}{2}x_0$ and σ is the crossing point. Applying the Laplace transformation to the population fluctuation

$$\delta\tilde{Q}(s) = \tau_L \int_0^\infty dt\, e^{-st}[Q(t) - Q^e]$$

$$= \frac{1}{2}(2\pi)^{1/4} \tau_L(\delta\tilde{a}_0^+ \pm \delta\tilde{a}_0^-)\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

$$= \left(\tau_0 - s\tau_1 + \frac{1}{2!}s^2\tau_2 - \cdots\right)\begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{47}$$

we obtain

$$\tau_n = \tau_L(-1)^n \frac{\partial^n}{\partial s^n} \delta\tilde{Q}(s)$$

$$= \tau_L(-1)^n \frac{\partial^n}{\partial s^n} \left[\frac{1}{2}(2\pi)^{1/4}(\delta\tilde{a}_0^+ \pm \delta\tilde{a}_0^-) \right] \tag{48}$$

Equation (44) can be written in matrix form as·

$$\frac{\partial}{\partial t} c_n = Q_n^- c_{n-1} + Q_n c_n + Q_n^+ c_{n+1} \tag{49}$$

where

$$c_n = (a_n^+, a_n^-, b_n^+, b_n^-)^T, \qquad n = 0, 1, 2,... $$

and

$$Q_n^- = \begin{bmatrix} 0 & \frac{-1}{2}x_0\sqrt{n} & 0 & 0 \\ \frac{-1}{2}x_0\sqrt{n} & 0 & 0 & 0 \\ 0 & 0 & 0 & b\sqrt{n} \\ 0 & 0 & b\sqrt{n} & 0 \end{bmatrix} \tag{50a}$$

$$Q_n = \begin{bmatrix} -n & 0 & 0 & 0 \\ 0 & -n & 0 & -a \\ 0 & 0 & -n & -b\sigma_y \\ 0 & \frac{1}{4}a & b\sigma_y & -n \end{bmatrix} \tag{50b}$$

$$Q_n^+ = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & b(n+1)^{1/2} \\ 0 & 0 & -b(n+1)^{1/2} & 0 \end{bmatrix} \tag{50c}$$

In solving Eq. (48), our procedure is to find Q^e first. Then we use Q^e to solve $\delta\tilde{a}_n^\pm$ and to find $\delta\tilde{a}_n^{\pm'}$, and so on.

At equilibrium, Eq. (49) is

$$Q_n^- c_{n-1} + Q_n c_n + Q_n^+ c_{n+1} = 0 \tag{51}$$

The Laplace transform of Eq. (51) gives

$$s\tilde{c}_n - c_n(0) = Q_n^- \tilde{c}_{n-1} + Q_n \tilde{c}_n + Q_n^+ \tilde{c}_{n+1} \tag{52}$$

Subtracting Eq. (52) from Eq. (51) and taking the limit $s \to 0$, we obtain

$$Q_n^- \, \delta\tilde{c}_{n-1} + Q_n \, \delta\tilde{c}_n + Q_n^+ \, \delta\tilde{c}_{n+1} = c_n(\infty) - c_n(0) \tag{53}$$

where

$$\delta\tilde{c}_n = \tilde{c}_n - \frac{c_n(\infty)}{s}$$

Differentiating with respect to s in Eq. (53) and letting $s \to 0$ yields

$$Q_n^- \, \delta\tilde{c}_{n-1}' + Q_n \, \delta\tilde{c}_n' + Q_n^+ \, \delta\tilde{c}_{n+1}' = \delta^{(0)}\tilde{c}_n \tag{54}$$

A similar procedure with Eqs. (51)–(53) leads to the algebraic equation for all higher-order differentiation $\delta\tilde{c}^{(i)}$:

$$Q_n^- \, \delta\tilde{c}_{n-1}^{(i)} + Q_n \, \delta\tilde{c}_n^{(i)} + Q_n^+ \, \delta\tilde{c}_{n+1}^{(i)} = n \, \delta\tilde{c}_n^{(i-1)} \tag{55}$$

Note that $\delta\tilde{c}^{(i)}$ depends on $\delta\tilde{c}^{(i-1)}$. In order to solve $\delta\tilde{c}^{(i)}$, we treat $\delta\tilde{c}^{(i-1)}$ as an initial condition. When $i = 1$, we have Eq. (54). The general equation that we need to solve can be expressed as

$$Q_n^- d_{n-1} + Q_n d_n + Q_n^+ d_{n+1} = e_n \tag{56}$$

where

$$d_n = \delta\tilde{c}_n^{(i)}, \qquad e_n = i \, \delta\tilde{c}_n^{(i-1)}$$

Define the ansatz $d_{n+1} = S_n^+ d_n + a_{n+1}$ and assume that $d_{N+1} = d_{N+2} = \cdots = 0$. When $n = N$,

$$\begin{aligned} S_{N-1}^+ &= -(Q_N)^{-1} Q_N^- \\ a_N &= (Q_N)^{-1} e_N \end{aligned} \tag{57}$$

Inserting this ansatz in Eq. (54), we obtain the following recurrence relations:

$$S_{n-1}^+ = -(Q_n + Q_n^+ S_n^+)^{-1} Q_n^- \tag{58a}$$

$$a_n = (Q_n + Q_n^+ S_n^+)^{-1} (e_{nn} - Q_n^+ a_{n+1}) \tag{58b}$$

Finally, we have all of the matrix elements

$$\begin{aligned} d_0 &= a_0 \\ d_1 &= S_0^+ d_0 + a_1 \\ d_2 &= S_1^+ d_1 + a_2 \end{aligned} \tag{59}$$

Since the inverse matrix of $a_0 = (Q_0 + Q_0^+ S_0^+)^{-1} (e_0 - Q_0^+ a_1)$ in Eq. (58b) with $n = 0$ is divergent, how do we find d_0 or a_0?

The first two elements of Eq. (58) are

$$Q_0 d_0 + Q_0^+ d_1 = e_0$$
$$d_1 = S_0^+ Q_0 + a_1$$

i.e.,

$$Q_0 d_0 + Q_0^+ (S_0^+ d_0 + a_1) = e_0 \tag{60a}$$

$$(Q_0 + Q_0^+ S_0^+) d_0 = e_0 - Q_0^+ a_1 \tag{60b}$$

Conservation of probability implies that the first component of e_0 (i.e., $e_{1,0}$) is zero. Note that we use δQ instead of using Q. The component form of Eq. (60b) has the structure

$$
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & x_{24} \\
x_{31} & x_{32} & x_{33} & x_{34} \\
x_{41} & x_{42} & x_{43} & x_{44}
\end{bmatrix}
\begin{bmatrix}
d_{1,0} \\
d_{2,0} \\
d_{3,0} \\
d_{4,0}
\end{bmatrix}
=
\begin{bmatrix}
0 \\
e_{2,0} \\
e_{3,0} \\
e_{4,0}
\end{bmatrix}
\tag{60c}
$$

From the probability conservation with the definition of

$$\rho_{11}(x, t) + \rho_{22}(x, t) = \sum_{n=0}^{\infty} a_n^+(t) \, r_n \left(\frac{x - \frac{1}{2} x_0}{\sqrt{2}} \right) \tag{61}$$

we obtain

$$\int_{-\infty}^{\infty} (\rho_{11}(x, t) + \rho_{22}(x, t)) = (2\pi)^{1/4} a_0^+(t) = 1 \tag{62a}$$

i.e.,

$$a_0^+(t) = (2\pi)^{-1/4} = \text{const} \tag{62b}$$

From the Laplace transform of the probability conservation

$$\int_0^{\infty} dt \, e^{-st} \int_{-\infty}^{\infty} dx \, (\rho_{11} + \rho_{22}) = \int_0^{\infty} dt \, e^{-st} [(2\pi)^{1/4} a_0^+(t)]$$

$$= \frac{1}{s} \tag{63}$$

along with the equilibrium condition $(2\pi)^{1/4} a_0^+(t=\infty)=1$, we have

$$\delta\tilde{c}_{1,0}^{(0)}(s) = \int_0^\infty dt\, e^{-st} \int_{-\infty}^\infty dx\, a_0^+(t)\, r_n\left(\frac{x-\frac{1}{2}x_0}{\sqrt{2}}\right) - \frac{1}{s}\left[(2\pi)^{1/4} a_0^+(t=\infty)\right]$$

$$= 0 \tag{64}$$

This implies that all of the higher-order terms vanish, i.e., $\delta\tilde{c}_{1,0}^{(i)}(s) = 0$, and $d_{1,0} = 0$ in Eq. (56) for any i.

Equation (60c) with $d_{1,0} = 0$ can easily be solved.

For the stationary solution, i.e., $e_n = 0$ for all n, we need to solve $Q_n^- c_{n-1} + Q_n c_n + Q_n^+ c_{n+1} = 0$. Let $S_n = c_{n+1}/c_n$; then we have

$$S_n = -[Q_{n+1} + Q_{n-1}^+ S_{n+1}]^{-1} Q_{n+1}^- \tag{65a}$$

$$c_n = S_{n-1} \cdots S_0 c_0 \tag{65b}$$

Here we truncate the system after the Nth term $(S_{N+1} = S_{N+2} = \cdots = 0$ and omit the equations with $n > N+1$).

How do we find the initial value c_0?

When $n = 0$, we have

$$Q_0 c_0 + Q_0^+ c_1 = 0$$

i.e.,

$$[Q_0 + Q_0^+ S_0]\, c_0 = 0 \tag{66}$$

It can be written in component form as $(c_0 = [R_{0,0}, R_{1,0}, R_{2,0}, R_{3,0}]^T)$

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \begin{bmatrix} R_{0,0} \\ R_{1,0} \\ R_{2,0} \\ R_{3,0} \end{bmatrix} = 0 \tag{67}$$

The combination of the normalization condition of $R_{i,0}$ and Eq. (67) leads to the solution of c_0 along with the fact that $R_{0,0} = a_0^+(\infty) = (2\pi)^{-1/4}$, i.e. $R_{0,0}$ should be rescaled to $(2\pi)^{-1/4}$. The moments which correspond to high frequency are easy to find. The Laplace transform of the basis set expansion of the population fluctuation is

$$\delta\tilde{Q}(s) = \int_0^\infty dt\, e^{-st} \int_{-\infty}^\infty dx\, \delta\rho(x,t)$$

$$= \sqrt{2}\,(2\pi)^{1/4} \int_0^\infty dt\, e^{-st}\, \delta a_0(t)$$

$$= \sqrt{2}\,(2\pi)^{1/4}\, \delta\tilde{a}_0(s) \tag{68}$$

From Eq. (46), the coefficient equation can be written in matrix notation as

$$\frac{\partial}{\partial t} \delta a(t) = M \, \delta a(0), \qquad a = (a_0^+, a_0^-, b_0^+, b_0^-; \ldots)^T \tag{69a}$$

i.e.,

$$\delta a(t) = e^{Mt} \, \delta a(0) \tag{69b}$$

Inserting Eq. (69b) in Eq. (68), we obtain

$$\delta \tilde{Q}(s) = \sqrt{2} \, (2\pi)^{1/4} \int_0^\infty dt \, e^{-(s - M)t} \, \delta a(0)$$

$$= \frac{1}{s} \sum_{i=0}^\infty \frac{1}{i!} \mu_i s^{-i} \tag{70}$$

Then we obtain all of the high-frequency moments as

$$\mu_i = (2\pi)^{1/4} \sqrt{2} \, M^i \, \delta a(0) \tag{71}$$

The moments can be solved successively, i.e.,

$$\mu_1 = \sqrt{2} \, (2\pi)^{1/4} \, \delta a(0)$$

$$\mu_2 = M \mu_1 \tag{72}$$

$$\cdots$$

The method that is developed in this paper to solve the generalized moments relies on the useful feature that M is a block tridiagonal matrix, where the blocks are 4×4 matrices, corresponding to the four coefficients $a_i^\pm$, $b_i^\pm$ for a given i.

4. NUMERICAL RESULTS

By using the method that we developed in ref. 10 and this paper, most of the long-time and short-time behavior of the nonadiabatic transition reaction can be obtained. We will compare the numerical calculation of the exact Zusman equation with the analytical result in this section.

4.1. Initial Condition

In this section, we show the effects of temperature, solvent dynamics, delocalization transition, electronic coupling, and transient time with
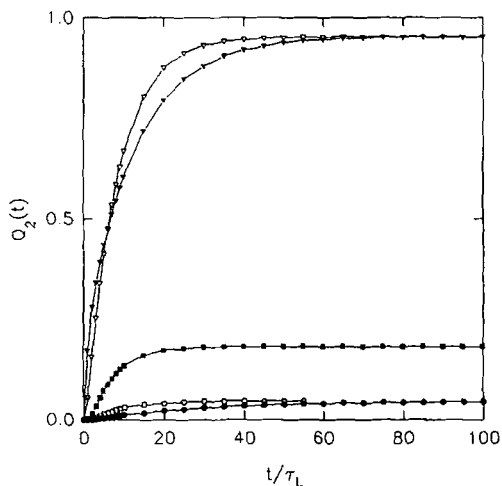
Fig. 2.   Population in well 2 as a function of delay time. In all of these curves we have $\hbar\omega_L = 100\ cm^{-1}$, $\lambda = 20$, $T = 300$ K, $a = 10$, $x_i = -2$, ($\bullet$) endothermic normal regime $S = 16.68$, $P = 6.256$; ($\square$) endothermic activationless regime $S = 6.256$, $P = 6.256$; ($\blacksquare$) endothermic inverted regime $S = 4.17$, $P = 3.128$; (∇) exothermic activationless regime $S = 6.256$, $P = -6.256$; ($\blacktriangledown$) exothermic inverted regime $S = 2.346$, $P = -6.256$.
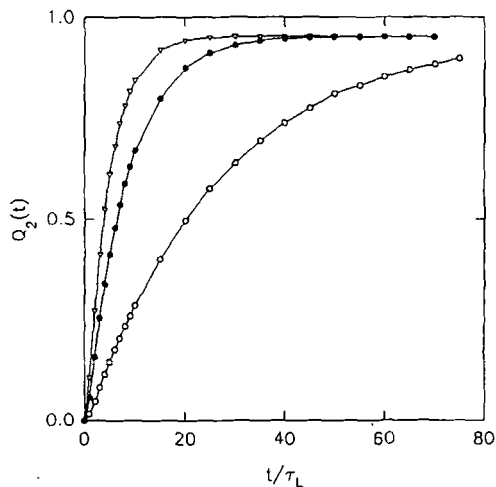
Fig. 3.   Population in well 2 as a function of delay time. The effect of the electronic coupling constant changes the delocalization width and increases the transition rate. The parameters that we used are $\hbar\omega_L = 100\ cm^{-1}$, $\lambda = 20$; $T = 300$ K; $x_i = -2$; ($\bigcirc$) $a = 5$; ($\bullet$) $a = 10$; (∇) $a = 15$.
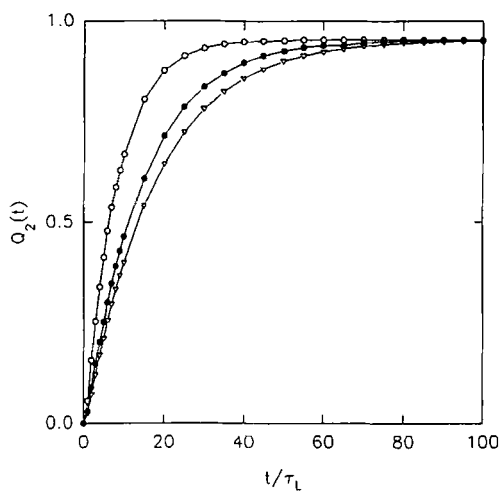
Fig. 4. The temperature effect on the population in well 2 as a function of delay time. We choose the parameters $\hbar\omega_L = 100 \text{ cm}^{-1}$, $\lambda = 20$, $a = 10$, $x_i = -2$; (∇) $T = 100$ K; ($\bullet$) $T = 300$ K; ($\bigcirc$) $T = 500$ K.
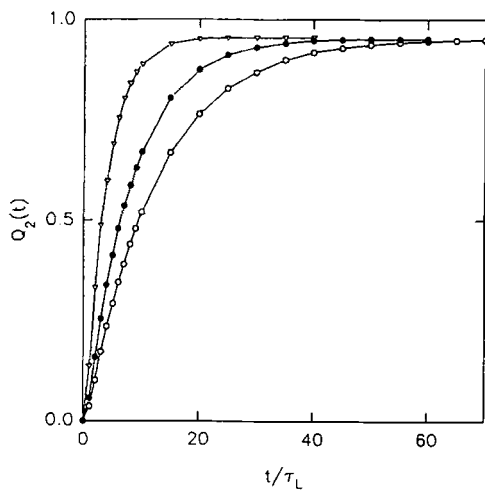

Fig. 5. Solvent dynamic effects on the population in well 2 as a function of delay time. We use the parameters $\hbar\omega_L = 100 \text{ cm}^{-1}$, $T = 300$ K, $a = 10$, $x_i = -2$; (∇) $\lambda = 50$; ($\bullet$) $\lambda = 40$; ($\bigcirc$) $\lambda = 10$.
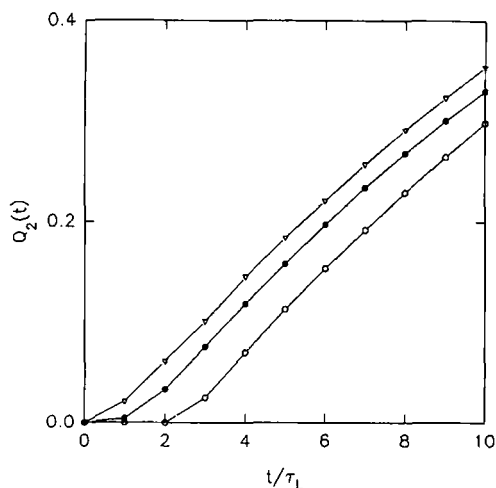
Fig. 6. Effect of transient time (t^*) in the activationless regime. The initial position is changed from -2, -4 to -6. We choose the parameters $\hbar\omega_L = 100 \text{ cm}^{-1}$, $T = 300$ K, $a = 10$, $\lambda = 60$; (∇) $x_i = -2$, $t^* = 0.4$; $(\bullet)$ $x_i = -4$, $t^* = 1.15$; $(\bigcirc)$ $x_i = -6$, $t^* = 2.5$.

far-from-equilibrium initial distribution. Since the difference between delta initial distribution and Gaussian initial distribution is small, we only show the delta initial distribution. Five different regimes are shown in Fig. 2. The probability distribution in well 2 is obtained by

$$Q_2(t) = [1 - (2\pi)^{1/4} a_0^-(t)] \tag{73}$$

The expansion coefficient $a_0^-(t)$ can be obtained by solving Eq. (46) with the Bulirsch–Stoer method[11] to integrate out $4 \times n$ $(n = 200)$ first-order differential equations. Fig. 3 shows the effect of the electronic coupling

Table I.   Comparison of Approximate and Exact Values of τ_0 and τ_1 [a]

		τ_0		τ_1	
S	P	Analytic	Numerical	Analytic	Numerical
1.68	6.256	1.38	1.35 (1.02)	37.33	34.876 (1.07)
6.256	6.256	0.525	0.51 (1.03)	4.5	4.23 (1.06)
4.17	3.128	1.68	1.62 (1.04)	11.61	10.5 (1.10)
6.256	−6.256	9.23	8.9 (1.04)	75.7	69.35 (1.09)

[a] $\hbar\omega_L = 100 \text{ cm}^{-1}$, $T = 300$ K, $x_i = -6$, $a = 10$, $\lambda = 20$. Values in parentheses are the ratios τ_{an}/τ_{num}.

constant in the activationless regime. The population increases rapidly in the short-time regime as a is increased. It shows that the delocalization width is increased as a is increased, because the temperature is in the low-temperature regime of the transition rate [see, for example, Eq. (38)]. In Fig. 4, the population in well 2 increases as the temperature is decreased. In Fig. 5, it is remarkable that the friction slows down the transition rate in the activationless regime and the effect is explicit before the equilibrium state is reached. Solvent dynamic effects make the transition localized. In Fig. 6, we show the effect of transient time in the activationless regime. The transient time, which is the time scale required for the initial distribution to relax to a sufficient population at the bottom of well 1, increases with increasing x_i.

4.2. Average Survival Time and Mean First Passage Time

The comparison of the numerical solution of τ_0 and τ_1 with the approximate analytic formulas given in (28) and (29) is presented in Table I. The parameters were chosen to correspond to the first four curves in Fig. 2. The effects of delocalization, temperature, solvent dynamics, and initial distribution are given in Table II. The diffusion rate constants k_{D1} and k_{D2} are obtained by direct integration of Eq. (33). The diffusion moment $k_{1,D1}^{ini}$ is obtained by integration of Eq. (34). The nonadiabatic rate constants k_{NA}^{12} and k_{NA}^{21} are defined by Eq. (32).

Table I shows that for an initial position x_i inside the transition region of sufficiently inverted regime the averaged survival time and mean first

Table II. Effect of Initial Distribution, Electronic Coupling Constant, Temperature, and Solvent Dynamics on τ_0 and τ_1 [a]

a	T	λ	x_i	τ_0	τ_1
5	300	20	−6	26.64	699.89
10	300	20	−6	8.9	69.34
15	300	20	−6	5.61	25.02
10	100	20	−6	4.8	17.57
10	300	20	−6	8.9	69.34
10	500	20	−6	12.9	153.84
10	300	10	−6	5.85	27.48
10	300	40	−6	14.89	208.4
10	300	50	−6	17.87	305.58
10	300	20	−2	7.87	60.46
10	300	20	−4	8.51	65.88
10	300	20	−6	8.9	69.35

[a] $\hbar\omega_L = 100 \text{ cm}^{-1}$, $T = 300$ K, $P = -6.256$, $S = -6.256$.

passage time cannot be broken up into the consecutive steps of diffusion in the donor well and surface crossing as shown in ref. 10. For the initial position outside the transition region and the regime not sufficiently inverted, Table I shows a good approximation of our analytic expression. The important feature is that the nuclear tunneling effect is included in k_{NA}. If we use the localized transition rate k_{NA}^{TST}, the results are completely incorrect.
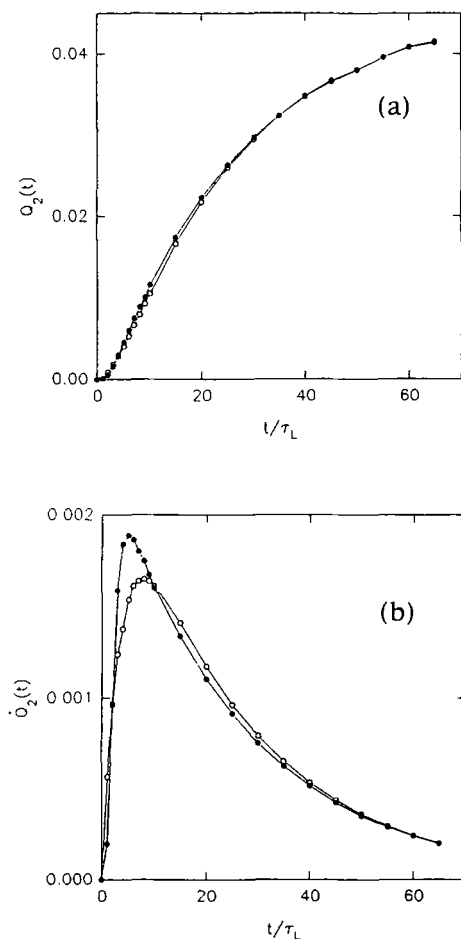

Fig. 7. Comparison between numerical ($\bullet$) and analytical ($\bigcirc$) calculations of (a) population and (b) reaction rate in well 2 with two relaxation times $\lambda_1^{-1} = 4.54$ and $\lambda_2^{-1} = 25.123$. Both plots correspond to $\hbar\omega_L = 100 \text{ cm}^{-1}$, $\lambda = 20$, $T = 300 \text{ K}$, $x_i = -2$, $a = 10$, $S = 16.68$, $P = 6.256$.

4.3. Multiexponential Relaxation

We compare the numerical calculation of $Q(t)$ and $\dot{Q}(t)$ from the approximate analytic formula (27) with the parameters based on four different regimes. The factors of the approximate analytic formula are evaluated by using a method similar to Section 4.2.
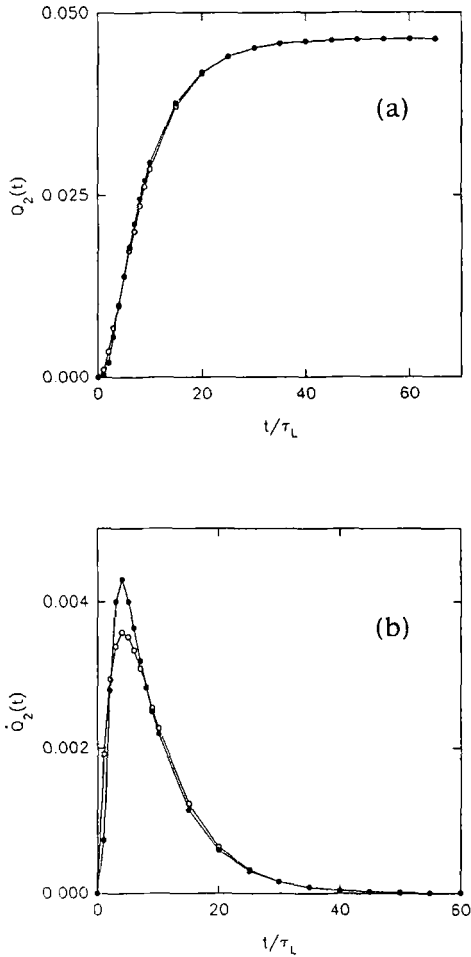

Fig. 8. Comparison between numerical ($\bullet$) and analytical ($\bigcirc$) calculations of (a) population and (b) reaction rate in well 2 with two relaxation times $\lambda_1^{-1} = 4.28$ and $\lambda_2^{-1} = 6.67$. Both plots correspond to $\hbar\omega_L = 100 \text{ cm}^{-1}$, $\lambda = 20$, $T = 300 \text{ K}$, $x_i = -2$, $a = 10$, $S = 6.256$, $P = 6.256$.

In Figs. 7, 8, 9 and 10, the long-time behavior of a two-relaxation-time description is very satisfactory. The short-time behavior can be fitted very well in the exothermic activationless regime. The reaction rate $(d/dt)\, Q_2(t)$ at $t = 0$ shows that a multiexponential decay time is needed in the nonadiabatic transition reaction. More than two-exponential decay in the normal and inverted regimes needs further study. For the normal and
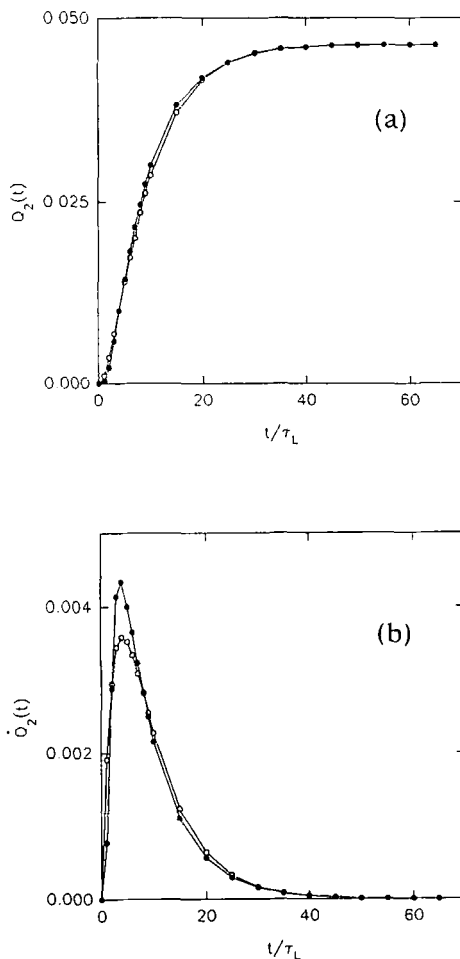

Fig. 9. Comparison between numerical (●) and analytical (○) calculations of (a) population and (b) reaction rate in well 2 with two relaxation times $\lambda_1^{-1} = 2.32$ and $\lambda_2^{-1} = 7.47$. Both plots correspond to $\hbar\omega_L = 100\ \mathrm{cm}^{-1}$, $\lambda = 20$, $T = 300\ \mathrm{K}$, $x_i = -2$, $a = 10$, $S = 4.17$, $P = 3.128$.

inverted regimes, the reaction rate cannot be fitted well at short time. This means that more short relaxation time scales should be included.

In conclusion, we have developed a systematic way to calculate the generalized moments with consecutive approximation. A new method is developed to simulate the numerical result. This method is much easier than the solution of the differential equation by the grid point method.
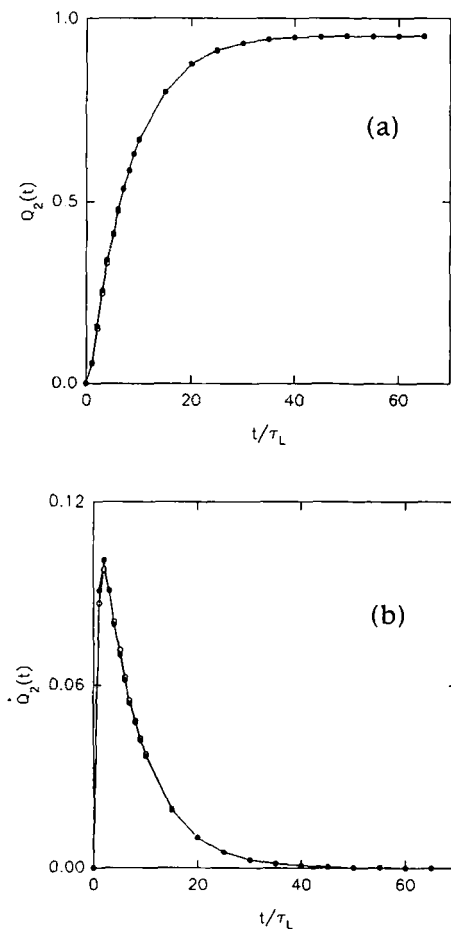

Fig. 10. Comparison between numerical ($\bullet$) and analytical ($\bigcirc$) calculations of (a) population and (b) reaction rate in well 2 with two relaxation times $\lambda_1^{-1} = 1.97$ and $\lambda_2^{-1} = 7.38$. Both plots correspond to $\hbar\omega_L = 100\,\text{cm}^{-1}$, $\lambda = 20$, $T = 300\,\text{K}$, $x_i = -2$, $a = 10$, $S = 6.256$, $P = -6.256$.

ACKNOWLEDGMENTS

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