Nonadiabatic transition at a level crossing with dissipation

Yosuke Kayanuma
Department of Mathematical Sciences, College of Engineering, Osaka Prefecture University, Sakai 599, Japan

Hiroyuki Nakayama
Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan
(Received 12 December 1997)

A comprehensive investigation of the transition dynamics of a level-crossing system with quantum dissipation is carried out for the Landau-Zener model coupled with a system of phonons. Analytical study by the formal perturbation expansion series with respect to the off-diagonal matrix element shows that the transition dynamics is characterized by the competition between the energy fluctuation and the energy dissipation. Closed expressions of the transition rate are derived for various limiting situations in a unified way. In the case of strong decoherence, a formula of the transition rate is obtained, which covers the high-temperature limit and the low-temperature, strong-coupling limit. Numerical calculation by utilizing the damping hyperoperator technique is performed, which clarifies the overall features of the time evolution of the system. [S0163-1829(98)03320-7]

I. INTRODUCTION

The nonadiabatic transition at a level crossing is a fundamental process that plays a crucial role in various aspects of the dynamical evolution of quantum systems. We may refer to a number of examples both in physics and chemistry. The best known is the atomic inelastic collisions with charge transfer.[1] The Born-Oppenheimer approximation breaks down around the avoided crossing of the potential curves associated with each charge state, and the nonadiabatic transition here is of primary importance in determining the branching ratio to respective scattering channels. Since the discovery of the celebrated Landau-Zener formula in 1932,[2,3] continuous effort has been devoted to elaborating the theoretical treatment.[4]

In the present paper, we focus our attention on the level-crossing problem in condensed matter. The nonradiative transitions in the strongly coupled localized electron-phonon system in solids is a typical example of this subject. In this case, the level crossing is defined in the configuration coordinate space instead of in the real space, and the nonradiative transition occurs during the lattice relaxation as the wave packet passes the crossing point of the adiabatic potentials.[5] The analysis of the transition dynamics by referring to the Landau-Zener formula has been done by several authors.[6–10] As another example, a sort of chemical reaction at the surface of crystals[11] and in the solvent[12] can be classified in this category, in which the nonadiabaticity of the process must be taken into account. It is pointed out that an analogous nonadiabatic level crossing is relevant in some nuclear reactions.[13] A slightly different version of the same problem can be found in the area of magnetic resonance[14] and in nonlinear optics.[15] By changing the applied magnetic fields or the electric fields, one can attain a level crossing between the two discrete levels. The so-called adiabatic rapid passage or its optical analogue has been analyzed in the framework equivalent to the Landau-Zener formula.[16,17] The quantum dynamics of a coupled spin system under a time-dependent magnetic field has been studied as a kind of nonadiabatic level-crossing problem.[18] The proposal to control the tunneling probability in the double-well potentials by periodically modulating the localized levels with the external fields[19] can also be regarded as coming in this category. In this connection, the effect of the environmental perturbation on the transition dynamics of a periodically driven system has been investigated by several authors.[20–23] The role of the phase coherence and its breakdown at successive crossing events is of special interest in this case. In some cases, the off-diagonal transfer element itself is induced by the coupling with the medium and, therefore, is fluctuating. The quantum dynamics of such a system has been studied for a level-crossing model[24] and for a biased two-level system.[25] Finally, we would like to add to our long but incomplete list of references an interesting *experimental* work,[26] in which it was demonstrated that a classical analogue of the repeated level crossing was realized in an optical-ring resonator and that the time-dependent behavior of the electromagnetic fields was well reproduced by the Landau-Zener model.

In contrast to the case of atomic collisions, the dynamical processes in condensed systems are, in many cases, subject to the perturbation by the elementary excitations in the surrounding media that have infinite degrees of freedom. The coupling with the surrounding media will generally modulate the transition rate at level crossings. One of the standpoints to investigate such an effect is to take the time-dependent model of Zener[3] coupled with a bath of many mode phonons. Although it may seem a little artificial to assume an explicit time dependence for the diabatic energies of the crossing levels, this model is useful to get insight into the essential dynamics of the nonadiabatic transitions at a single crossing event, and it is called a standard model. The effect of the environmental perturbation in the level-crossing problem has been investigated by several authors within the standard model.[27–30] From the theoretical point of view, this problem gives an interesting time-dependent version of the quantum tunneling with dissipation.[31,32] See Leggett *et al.*[33] for a re-

view on the dynamics of the dissipative two-level system and references therein.

We would like to emphasize here that the concept of quantum dissipation should be understood from two distinct viewpoints. One is the dissipation of energy and the other is the fluctuation of energy, or in other words, the dissipation of the phase memory. The relative magnitudes of the effects of these mechanisms are connected to each other through the fluctuation-dissipation theorem. One of the present authors investigated the effect of the phase relaxation on the transition probability by reducing the standard model to a stochastic model at high temperature.[28] It was shown that the existence of the phase relaxation generally increases the apparent nonadiabaticity. Especially, a closed formula of the transition rate was obtained in the limit of strong dephasing, which shows an incoherent or a diffusionlike transfer. Ao and Rammer[30] developed an extensive analysis for the original standard model. They obtained analytical expressions of the transition rate for some extreme cases of the parameter values. A remarkable conclusion is that the effect of the environmental perturbation on the transition rate disappears at low temperatures in the case that the system starts from the lower branch in the initial state. This assertion is not consistent with the previous result of the analytical study in the same model,[29] in which the authors investigated the transition process from the adiabatic limit and concluded that, at zero temperature, the coupling with the phonon fields *decreases* the apparent nonadiabaticity.

On the other hand, a numerical calculation of the transition dynamics was done by Tsukada[27] for a semiclassical version of the standard model by utilizing the stochastic-trajectory method. It was clearly shown in this work that, because of the back-transfer effect, the energy relaxation dramatically modifies the transition rate in the case that the system initially occupies the upper level. The validity of the approximation adopted to derive the force term in the stochastic equation is, however, not always justified since the environmental oscillators are assumed as being driven by a common force irrespective of the electronic subspace. This is a drawback often seen in this type of calculation. Note that the Hellmann-Feynman force is well defined only for the adiabatic eigenstates.

In view of this situation, it will be worthwhile to carry out a further study of this subject. The purpose of the present work is to make a comprehensive investigation of the level-crossing problem in condensed matter within the framework of the standard model, both analytically and numerically. By the analysis of the formal perturbation expansion series, closed expressions of the transition rate, some of which have been obtained previously, are derived in a unified way. Specifically, a formula is obtained that covers the limit of the strong-phase relaxation, bridging the high-temperature limit and the low-temperature limit. In order to clarify the features of the transition dynamics all over the parameter space, we perform a numerical investigation utilizing the damping hyperoperator technique. Through the numerical calculation of the time-dependent behavior of the reduced density matrix, it is clearly seen what is going on in the electronic system during the level crossing under the influence of the quantum dissipation. In the extreme cases of the parameter values, the results of the analytical formulas are ascertained. In addition, a peculiar feature of the damping operator technique as a tool for such a calculation is also critically examined.

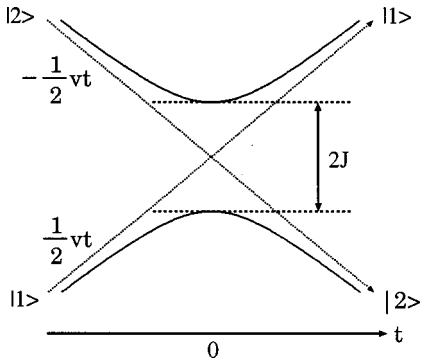

FIG. 1. The Landau-Zener model of level crossing.

In Sec. II, the model is presented with some remarks about the physical parameters. The analytical study is carried out in Sec. III. Section IV is devoted to the introduction of the interaction mode and the formulation of the damping operator method. The results of the numerical calculation are presented in Sec. V. Some concluding comments are given in Sec. VI.

II. MODEL

We are interested in the transition dynamics at a level crossing as an elementary process of the evolution of a quantum system. Consider that the energy levels of two electronic states, $|1\rangle$ and $|2\rangle$, approach and cross each other as shown in Fig. 1 in accordance with the motion of a heavy degree of freedom or by an external modulation. The system initially exists in $|1\rangle$ makes a transition to $|2\rangle$ through a constant off-diagonal matrix element J around the crossing. Throughout this paper, we choose diabatic basis set $|1\rangle$ and $|2\rangle$ to define the *transition*. The whole system is assumed as being subject to the perturbation by the elementary excitations in the surrounding medium represented by phonons. By extending Zener's model, a prototype Hamiltonian to discuss the situation can be written as

$$H(t)=H_{\mathrm{el}}(t)+H_{\mathrm{ph}}+H_I, \tag{1}$$

$$H_{\mathrm{el}}(t)=\tfrac{1}{2}vt(|1\rangle\langle 1|-|2\rangle\langle 2|)+J(|1\rangle\langle 2|+|2\rangle\langle 1|), \tag{2}$$

$$H_{\mathrm{ph}}=\sum_k \omega_k b_k^\dagger b_k, \tag{3}$$

$$H_I=\tfrac{1}{2}\sum_k \alpha_k\omega_k(b_k+b_k^\dagger)(|1\rangle\langle 1|-|2\rangle\langle 2|), \tag{4}$$

where v is the velocity of the change of the energy difference, α_k is the coupling constant with the kth phonon mode of frequency ω_k. Here and hereafter we adopt $\hbar=1$. It is assumed that at $t=-\infty$, the total system is represented by the density matrix ρ_i given by

$$\rho_i=|1\rangle\langle 1|\rho_1, \tag{5}$$

where ρ_1 represents the phonon equilibrium in the subspace $|1\rangle$, namely,

$$\rho_1=\exp(-H_1/k_BT)/\mathrm{Tr}\,\exp(-H_1/k_BT), \tag{6}$$

with

$$H_1=H_{\mathrm{ph}}+\tfrac{1}{2}\sum_k \alpha_k\omega_k(b_k+b_k^\dagger). \tag{7}$$

We calculate the probability P that the electronic system exists in $|2\rangle$ at $t=\infty$. Note that the transition rate depends also on the sign of v unlike the original Landau-Zener model.

Because of the Gaussian character of the linear electron-phonon interaction, the dynamics of the quantum dissipation can be completely specified by the spectral-density function $\phi(\omega)$ defined by

$$\phi(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle V(t)V(0)\rangle_0 e^{i\omega t}dt$$

$$=\sum_k \alpha_k^2\omega_k^2[(n_k+1)\delta(\omega-\omega_k)+n_k\delta(\omega+\omega_k)], \tag{8}$$

where

$$V\equiv\sum_k \alpha_k\omega_k(b_k+b_k^\dagger),\quad V(t)\equiv\exp(iH_{\mathrm{ph}}t)V\exp(-iH_{\mathrm{ph}}t),$$

and $n_k\equiv 1/\{\exp(\omega_k/k_BT)-1\}$. In the above equation, $\langle\cdots\rangle_0$ is the average over the density matrix $\rho_0\equiv\exp(-H_{\mathrm{ph}}/k_BT)/\mathrm{Tr}\exp(-H_{\mathrm{ph}}/k_BT)$.

The relaxation energy ΔE is given by

$$\Delta E=\int_{-\infty}^{\infty}\phi(\omega)\omega^{-1}d\omega, \tag{9}$$

which is half of the Stokes shift for the optical transition. The amplitude of the energy fluctuation D is given by

$$D^2=\int_{-\infty}^{\infty}\phi(\omega)d\omega. \tag{10}$$

We define the dimensionless coupling constant S by

$$S=\sum_k \alpha_k^2 \tag{11}$$

and the representative phonon energy $\bar{\omega}$ by

$$\Delta E=S\bar{\omega}. \tag{12}$$

The transition dynamics is insensitive to the detailed functional form of $\phi(\omega)$ but is characterized by the parameters v, J, $\bar{\omega}$, S, and k_BT. It should be noted that ΔE and D are related to each other through the Einstein relation

$$D^2\simeq 2k_BT^*\Delta E, \tag{13}$$

where, recovering $\hbar$, $T^*\equiv(\hbar\bar{\omega}/2k_B)\coth(\hbar\bar{\omega}/2k_BT)$ is the effective temperature. Therefore, the effect of the energy fluctuation becomes dominant while the energy dissipation can be neglected in the limit of weak coupling and high temperature,

$$\Delta E\to 0,\quad k_BT\to\infty\quad\text{with}\quad D\ \text{finite}. \tag{14}$$

This is the case described well by the stochastic model.[28] On the other hand, in the limit of strong coupling and low temperature, the effect of the energy relaxation as well becomes important since in this limit,

$$\bar{\omega}\ll D\simeq\sqrt{S}\bar{\omega}\ll\Delta E. \tag{15}$$

The stochastic fluctuation of the energy difference generally leads to the phase relaxation. In the case that $D/\bar{\omega}\gg 1$, the relative-phase memory is completely lost within a short time of order of $\tau_{\mathrm{ph}}\simeq D^{-1}(\ll\bar{\omega}^{-1})$. For $D/\bar{\omega}\lesssim 1$, the phase relaxation is incomplete. This is a feature of the linear coupling model and is connected with the presence of a sharp zero-phonon line in the optical-transition spectrum.

The time constant τ_{en} of the relaxation of the energy is given by $\tau_{\mathrm{en}}\simeq\gamma_p^{-1}$, where γ_p is the width of $\phi(\omega)$ at low temperature. In most cases, γ_p is roughly the same order of magnitude as $\bar{\omega}$ itself. The time constants τ_{ph} and τ_{en} should be compared with the time interval τ_{tr} within which the system exists in the transition region. Since the off-diagonal coupling works for the energy difference of order of or less than J, τ_{tr} is primarily given by, in the order of magnitude,

$$\tau_{\mathrm{tr}}\simeq J/|v|, \tag{16}$$

for moderate values of J. As shown in the next section, the whole transition process is characterized by the degree of coherence, which is measured by the ratio of τ_{ph} and τ_{tr}.

III. ANALYTICAL CONSIDERATION

In this section, we investigate the transition dynamics analytically by the formal perturbation expansion series of P. The density matrix $\rho(t)$ at time t is given by

$$\rho(t)=\exp_+\left[-i\int_{-\infty}^{t}H(\tau)d\tau\right]\rho_i\exp_-\left[i\int_{-\infty}^{t}H(\tau')d\tau'\right], \tag{17}$$

where $\exp_+$ ($\exp_-$) means the time-ordered exponential with increasing time toward left (right). The probability P is then given by

$$P=\left\langle\left\{\exp_-\left[i\int_{-\infty}^{\infty}H(\tau')d\tau'\right]\right\}_{1,2}\times\left\{\exp_+\left[-i\int_{-\infty}^{\infty}H(\tau)d\tau\right]\right\}_{2,1}\right\rangle_1, \tag{18}$$

in which $\{\cdots\}_{i,j}$ means that the (i,j) component should be taken and $\langle\cdots\rangle_1$ indicates the expectation value over the equilibrium phonon in the space $|1\rangle$,

$$\langle\cdots\rangle_1\equiv\mathrm{Tr}\{\rho_1\cdots\}. \tag{19}$$

The probability P is expanded in a power series of J to infinite orders. Each term is expressed as a sum of multiple time-ordered integrals of higher-order generating functions. The calculation of the generating functions is essentially an elementary exercise. Analytical expressions of the same kind have been derived time and again by several authors within different contexts.[8–10,32] We present here a compact form,

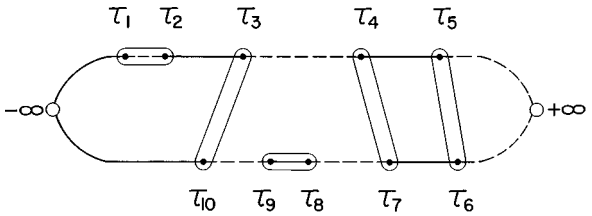

FIG. 2. The double-path Feynmann diagram for a $2n$th-order term of the perturbation expansion series of the probability P. The system makes a transition at each vertex from $|1\rangle$ (solid line) to $|2\rangle$ (dashed line) and vice versa. In the limit of large amplitude fluctuation, time vertices encircled by the ellipses must be paired off.

$$P=-\sum_{n=1}^{\infty}(-J^2)^n L^{(n)}, \tag{20}$$

$$\begin{aligned}L^{(n)}=&\sum_{m=1}^{n}\int_{-\infty}^{\infty}d\tau_1\int_{\tau_1}^{\infty}d\tau_2\cdots\int_{\tau_{2m-2}}^{\infty}d\tau_{2m-1}\\&\times\int_{-\infty}^{\infty}d\tau_{2m}\int_{-\infty}^{\tau_{2m}}d\tau_{2m+1}\cdots\int_{-\infty}^{\tau_{2n-1}}d\tau_{2n}\\&\times\exp\left[i\sum_{j=1}^{2n}(-1)^j\left(\frac{v}{2}\tau_j^2-\Delta E\tau_j\right)\right.\\&\left.+\sum_{i=2}^{2n}\sum_{j=1}^{i-1}(-1)^{i+j}G(\tau_i-\tau_j)\right],\end{aligned} \tag{21}$$

where

$$\begin{aligned}G(t)\equiv&\int_0^t ds\int_0^\tau ds'\langle V(s)V(s')\rangle_0\\=&\int_{-\infty}^{\infty}d\omega\,\phi(\omega)[(1-e^{-i\omega t})\omega^{-2}-it\omega^{-1}].\end{aligned} \tag{22}$$

The diagrammatic representation of the above expression is shown in Fig. 2 as a double-path propagator for the density matrix.

We note that the lowest-order term of P coincides with that of the Landau-Zener formula irrespective of the phonon coupling[28,30] since

$$\begin{aligned}L^{(1)}=&\int_{-\infty}^{\infty}d\tau_1\int_{-\infty}^{\infty}d\tau_2\\&\times\exp\left[i\frac{v}{2}(\tau_2^2-\tau_1^2)-i\Delta E(\tau_2-\tau_1)-G(\tau_2-\tau_1)\right]\\=&\int_{-\infty}^{\infty}d\mu\int_{-\infty}^{\infty}d\sigma\,\exp[iv\sigma\mu-i\Delta E\sigma-G(\sigma)]=\frac{2\pi}{|v|},\end{aligned} \tag{23}$$

where we have introduced new variables, $\mu\equiv(\tau_1+\tau_2)/2$ and $\sigma\equiv\tau_2-\tau_1$. It is difficult to evaluate the multiple integrals for general terms. However, the meaning of formula (21) becomes clear in the limit of large amplitude fluctuation $D/\overline{\omega}\gg 1$, namely, in the limit of strong coupling and/or high temperature. The following theorem is of primary importance for the analysis of the dynamical process in this limit.[34]

Pairing-off theorem. Out of all the configurations of the time vertices that appear in the diagrams shown in Fig. 2, only those make nonvanishing contributions to the integral in Eq. (21), in which $2n$ vertices make pairs with intrapair distance less than D^{-1} except for special cases in which an even number of vertices not less than four make groups with mutual distance less than $(\overline{\omega}D)^{1/2}$.

Proof. In order to prove the theorem, we divide the exponent of the generation function in Eq. (21) into the real part $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ and the imaginary part $I(\tau_1,\tau_2,\ldots,\tau_{2n})$. The real part

$$R(\tau_1,\tau_2,\ldots,\tau_{2n})=\mathrm{Re}\sum_{i=2}^{2n}\sum_{j=1}^{i-1}(-1)^{i+j}G(\tau_i-\tau_j)$$

originates from the fluctuation of the energy. We observe that $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ can be rewritten as

$$\begin{aligned}R(\tau_1,\tau_2,\ldots,\tau_{2n})=&-\frac{1}{2}\int_{-\infty}^{\infty}d\omega\,\phi(\omega)\omega^{-2}\\&\times\left|\sum_{j=1}^{2n}(-1)^j e^{i\omega\tau_j}\right|^2.\end{aligned} \tag{24}$$

Note that $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ is a nonpositive definite quantity. Since

$$\int_{-\infty}^{\infty}d\omega\;\phi(\omega)\omega^{-2}\simeq D^2/\overline{\omega^2}\gg 1,$$

$R(\tau_1,\tau_2,\ldots,\tau_{2n})$ becomes negative with a large absolute value unless the following condition is satisfied:

$$\left|\sum_{j=1}^{2n}(-1)^j e^{i\omega\tau_j}\right|\lesssim\overline{\omega}/D. \tag{25}$$

Since the integral with respect to ω runs over the interval of order of γ_p, the above condition is satisfied in the limit $D/\overline{\omega}\to\infty$ only when $2n$ vertices are paired off, namely, a time vertex with even suffix coincides with a time vertex with odd suffix to be canceled out as shown in Fig. 2. By expanding the expression $\Sigma_{j=1}^{2n}(-1)^j e^{i\omega\tau_j}$ in a power series around the paired-off configuration, the theorem is immediately proved.

The pairing-off property of the strongly coupled localized electron-phonon system has been described by Kusunoki[8] in a less clear way. Sumi[9] correctly stated the pairing-off ansatz in his study of the nonradiative process in solids, but the context in which it was used was inappropriate. See Sec. VI for more details. The pairing-off theorem plays an essential role in understanding the dual character of the Raman scattering and the luminescence in the second-order optical process of the strongly coupled electron-phonon system.[34]

The above theorem provides a mathematical basis for the *noninteracting blip approximation*,[32] which is widely used in the study of the dynamics of the spin-boson system. In its lowest order, the noninteracting blip approximation requires us to simply drop all the terms $G(\tau_i-\tau_j)$ that extend over different pairs.[33] By this approximation, the memory of the boson system about the previous history is instantly lost at

each blip. In order to correctly describe the energy relaxation, which is important in the strong-coupling limit, the history must be taken into account as the interaction between blips.

The pairing-off theorem is a consequence of the ultrafast phase relaxation in the large-amplitude fluctuation limit. As can be seen from Fig. 2, the density matrix propagates almost always in the diagonal form in this limit. In the remaining part of this section, we mainly focus our attention on this limit.

If one notices that

$$\sum_{i=2}^{2n}\sum_{j=1}^{i-1}(-1)^{i+j}(\tau_i-\tau_j)=-\sum_{j=1}^{2n}(-1)^j\tau_j,$$

the imaginary part $I(\tau_1,\tau_2,\ldots,\tau_{2n})$ of the exponent of Eq. (21) can be rewritten as

$$I(\tau_1,\tau_2\ldots,\tau_{2n})=\frac{v}{2}\sum_{j=1}^{2n}(-1)^j\tau_j^2-\int_{-\infty}^{\infty}d\omega\ \phi(\omega)\omega^{-2}\times\sum_{i=2}^{2n}\sum_{j=1}^{i-1}\sin\omega(\tau_i-\tau_j). \quad (26)$$

We classify the paired configuration into two groups: the vertical pairs and the horizontal pairs. The vertical pair lies across the upper and the lower propagator like pairs (τ_3,τ_{10}), (τ_7,τ_4), and (τ_5,τ_6) in Fig. 2. The horizontal pair lies within the upper or the lower propagator like (τ_1,τ_2) and (τ_9,τ_8). Denote the pairs as $(\tau_{\lambda_1},\tau_{\lambda_2})$, $(\tau_{\lambda_3},\tau_{\lambda_4}),\ldots,(\tau_{\lambda_{2n-1}},\tau_{\lambda_{2n}})$ as they are ordered from left toward right, where we take $\lambda_{2m-1}=$odd and $\lambda_{2m}=$even. Introduce a set of new variables as

$$\mu_m=(\tau_{\lambda_{2m}}+\tau_{\lambda_{2m-1}})/2,\quad \sigma_m=\tau_{\lambda_{2m}}-\tau_{\lambda_{2m-1}}. \quad (27)$$

Then in the limit $D/\overline{\omega}\gg 1$, the saddle-point method can be applied to the evaluation of the multiple time-ordered integrals by expanding $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ and $I(\tau_1,\tau_2,\ldots,\tau_{2n})$ to the lowest order in σ_m. The real part can be readily approximated as

$$R(\tau_1,\tau_2,\ldots,\tau_{2n})\simeq-\frac{1}{2}\int_{-\infty}^{\infty}d\omega\ \phi(\omega)\times\sum_{p=1}^{n}\sum_{q=1}^{n}\cos\omega(\mu_p-\mu_q)\sigma_p\sigma_q. \quad (28)$$

On the other hand, the imaginary part can be evaluated by an elementary but somewhat tedious counting up of the diagram and by some exercise of trigonometry as

$$I(\tau_1,\tau_2,\ldots,\tau_{2n})\simeq\sum_{p=1}^{n}E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)\sigma_p, \quad (29)$$

where $E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)$ is given by

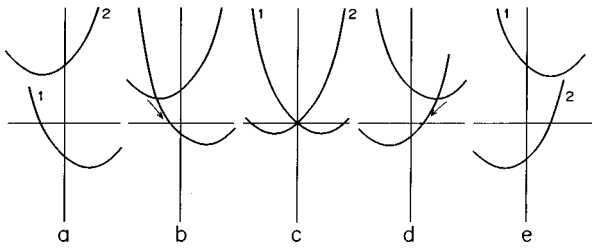

FIG. 3. The schematic time evolution of the configuration coordinate diagram for the level crossing with energy relaxation. The time evolution is from (a) to (e) in the case $v>0$ and from (e) to (a) in the case $v<0$.

$$E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)=v\mu_p+(-1)^{(q+1)}\Delta E+2\sum_{j=1}^{q}(-1)^j\times\int_{-\infty}^{\infty}d\omega\ \phi(\omega)\omega^{-1}\cos\omega(\mu_p-\mu_j). \quad (30)$$

In the above equation, $\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q}$ are the times for the vertical pairs that lie to the left of μ_p in Fig. 2. For the case that there is no vertical pair before μ_p, $E_p^{(q)}$ should read as $E_p^{(0)}\equiv v\mu_p-\Delta E$. Although the derivation is somewhat complicated, the meaning of the above formula is obvious. The energy $E_p^{(q)}$ is nothing but the negative value of the Franck-Condon energy measured from $|1\rangle$ to $|2\rangle$ for the phonon wave packet, which has the following history: it starts from the equilibrium distribution in the subspace $|1\rangle$, makes a vertical transition to the adiabatic potential surface of $|2\rangle$ at time μ_{v_1}, is driven by the Hamiltonian within the subspace $|2\rangle$ until the time μ_{v_2} at which it jumps again to the adiabatic potential surface of $|1\rangle$, and so on. For q even, the packet lies on the adiabatic potential surface in $|1\rangle$ and for q odd, in $|2\rangle$. Therefore, it can be said that the vertical pair corresponds to the *transition* while the horizontal pair corresponds to the *polarization*. At each time the system makes a transition, the equilibrium point of the phonon system shifts from left to right and vice versa. Such a situation may be visualized by the configuration coordinate diagram as shown in Fig. 3. The meaning of the coordinate in Fig. 3 will be made clear in the next section.

Now we come to the point of a crucial observation. So far, we have not considered the time duration $\tau_{\rm tr}$ within which the system exists in the transition region. The time $\tau_{\rm tr}$ is a measure of the time interval for which the multiple integral of Eq. (21) converges. On the other hand, the pairing-off theorem tells us that the contribution from the integral over σ_p for each pair is restricted within the time interval $|\sigma_p|\lesssim\tau_{\rm ph}(\simeq D^{-1})$ in the order of magnitude. The transition associated with each pair becomes a *real* transition only in the case that the phase relaxation time is far less than the transition time, namely, $\tau_{\rm ph}\ll\tau_{\rm tr}$.

First, we consider the opposite case that the velocity $|v|$ is so large that the condition $\tau_{\rm ph}\gg\tau_{\rm tr}$ is satisfied. In this case, the real part $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ given in Eq. (24) can be approximated as

$$R(\tau_1,\tau_2,\ldots,\tau_{2n}) = -\frac{1}{2}D^2\left(\sum_{p=1}^{n}\sum_{q=1}^{n}\sigma_p\sigma_q\right) = -\frac{1}{2}D^2\left\{\sum_{j=1}^{2n}(-1)^j\tau_j\right\}^2, \quad (31)$$

since $|\mu_p-\mu_q| \ll \gamma_p^{-1}$ for all p and q. Likewise, the imaginary part can be approximated simply as

$$I(\tau_1,\tau_2,\ldots,\tau_{2n}) = \tfrac{1}{2}v\sum_{j=1}^{2n}(-1)^j\tau_j^2. \quad (32)$$

Equation (31) means that the fluctuation of the energy behaves as a static Gaussian distribution of the energy for a very short time interval. In fact, the effect of $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ can be eliminated from the integral of Eq. (21) by applying the identity

$$\exp[-D^2X^2/2] = (\sqrt{2\pi}D)^{-1}\int_{-\infty}^{\infty}dq\ \exp[-q^2/2D^2 - iqX] \quad (33)$$

for $X \equiv \Sigma_{j=1}^{2n}(-1)^j\tau_j$ and by interchanging the order of the integration over q and τ_j with the shift of the origin $\tau_j \to \tau_j - q/v$. This is a consequence of the feature of the Landau-Zener model that the transition rate is independent of the constant shift of the relative energy.

It is instructive to calculate $L^{(n)}$ explicitly in this limit. By an inspection of the integral domain, $L^{(n)}$ can be rewritten as

$$L^{(n)} = \sum_{m=0}^{n} C_m C_{n-m}^*, \quad (34)$$

where

$$C_0 = 1,$$

$$C_m = \int_{-\infty}^{\infty}d\tau_1\int_{\tau_1}^{\infty}d\tau_2\cdots\int_{\tau_{2m-1}}^{\infty}d\tau_{2m} \times\exp\left[i\frac{v}{2}\sum_{j=1}^{2m}(-1)^j\tau_j^2\right], \quad m\geqslant 1. \quad (35)$$

The following transformation of the variables is useful for the evaluation of the ordered integral,[17]

$$x_1 = \tau_1,$$

$$x_p = \tau_1 + \sum_{j=1}^{p-1}(\tau_{2j+1}-\tau_{2j}), \quad 2\leqslant p\leqslant m,$$

$$y_p = \tau_{2p}-\tau_{2p-1}, \quad 1\leqslant p\leqslant m, \quad (36)$$

by which C_m is written as

$$C_m = \int_{-\infty}^{\infty}dx_1\int_{x_1}^{\infty}dx_2\cdots\int_{x_{m-1}}^{\infty}dx_m \times\int_0^{\infty}dy_1\int_0^{\infty}dy_2\cdots\int_0^{\infty}dy_m \times\exp\left[iv\sum_{p=1}^{m}x_py_p + \frac{iv}{2}\left(\sum_{p=1}^{m}y_p\right)^2\right]. \quad (37)$$

Since the integral is unchanged by arbitrary permutations of $(x_1,x_2,\ldots,x_n)$, the integration is carried out as

$$C_m = \frac{1}{m!}\int_{-\infty}^{\infty}dx_1\int_{-\infty}^{\infty}dx_2\cdots\int_{-\infty}^{\infty}dx_m \times\int_0^{\infty}dy_1\int_0^{\infty}dy_2\cdots\int_0^{\infty}dy_m \times\exp\left[iv\sum_{p=1}^{m}x_py_p + \frac{iv}{2}\left(\sum_{p=1}^{m}y_p\right)^2\right] = \frac{1}{m!}\left(\frac{\pi}{|v|}\right)^m, \quad (38)$$

where the second equality is obtained by first performing the integrations over x_p. Inserting the above result into Eq. (34), we find

$$L^{(n)} = \frac{1}{n!}\left(\frac{2\pi}{|v|}\right)^n, \quad (39)$$

and inserting this into Eq. (20), we obtain the Landau-Zener (LZ) formula,

$$P = P_{\mathrm{LZ}} \equiv 1-\exp(-2\pi J^2/|v|). \quad (40)$$

The argument here was the essence of the proof of the applicability of the Landau-Zener formula to the nonradiative hot transitions in the strongly coupled localized electron-phonon system with an adiabatic potential crossing.[10]

Next, we turn to the limit of slow passage, $\tau_{\mathrm{tr}} \gg \tau_{\mathrm{ph}}$. In this case, the coherence is interrupted every moment in the relatively long time interval τ_{tr} and the vertical pairs in Fig. 2 can be interpreted as representing real transitions. The system makes multiple transitions between $|1\rangle$ and $|2\rangle$ while relaxing toward the equilibrium state within the respective electronic subspace. Therefore, the probability P would depend on the relative length of τ_{tr} and τ_{en}. Useful expressions of P can be obtained in the case that a little stronger condition

$$\tau_{\mathrm{tr}} > \tau_{\mathrm{en}} \quad (41)$$

is satisfied. In this case, $R(\tau_1,\tau_2,\ldots,\tau_{2n})$ can be approximated as

$$R(\tau_1,\tau_2,\ldots,\tau_{2n}) = -\frac{1}{2}D^2\left(\sum_{p=1}^{n}\sigma_p^2\right), \quad (42)$$

since the cross terms vanish because of the dephasing,

$$\int d\omega\ \phi(\omega)\omega^{-1}\cos\omega(\mu_p-\mu_q) \simeq 0,$$

for general configurations of μ_p and μ_q with $|\mu_p-\mu_q| \simeq O(\tau_{\rm en})$. The variables of integration are changed from $(\tau_1,\tau_2,\ldots,\tau_{2n})$ to $(\mu_1,\mu_2,\ldots,\mu_n,\sigma_1,\sigma_2,\ldots,\sigma_n)$. We assign a set of signatures $(\xi_1,\xi_2,\ldots,\xi_n)$ to each diagram corresponding to a serial time ordering, where $\xi_m=+1$ if $\tau_{\lambda_{2m-1}}<\tau_{\lambda_{2m}}$ and $\xi_m=-1$ if $\tau_{\lambda_{2m}}<\tau_{\lambda_{2m-1}}$. For example, $(\xi_1,\xi_2,\xi_3,\xi_4,\xi_5)=(+1,-1,+1,-1,+1)$ in the case of time ordering in Fig. 2. Then, the following lemma can be proved by an elementary counting up of the diagram.[28]

Lemma 1. In the total set of possible time ordering that appears in the $2n$th-order terms of the perturbation expansion, every set $(\xi_1,\xi_2,\ldots,\xi_n)$ with $\xi_p=\pm1$ for $p=1,2,\ldots,n$ appear 2^{n-1} times.

Since the integral over σ_p converges for $|\sigma_p|\lesssim\tau_{\rm ph}$, the restriction on the integral domain for μ_p can be safely relaxed as $-\infty<\mu_1\leqslant\mu_2\leqslant\cdots\leqslant\mu_n<\infty$. On the other hand, the integral domain of σ_p can be extended to $-\infty<\sigma_p<\infty$ for the vertical pairs and to $0\leqslant\sigma_p<\infty$ or $-\infty<\sigma_p\leqslant0$ for the horizontal pairs.

First, we calculate P for the case that the energy dissipation is negligible, $\Delta E\to0$, while the condition $D/\overline{\omega}\gg1$ is still satisfied. This corresponds to the high-temperature limit with small coupling. The imaginary part $I(\tau_1,\tau_2,\ldots,\tau_{2n})$ can be written as

$$I(\tau_1,\tau_2,\ldots,\tau_{2n})=v\sum_{p=1}^{n}\mu_p\sigma_p, \tag{43}$$

and, because of the above lemma, we find

$$\begin{aligned}L^{(n)}&=2^{n-1}\int_{-\infty}^{\infty}d\mu_1\int_{\mu_1}^{\infty}d\mu_2\cdots\int_{\mu_{n-1}}^{\infty}d\mu_n\\&\quad\times\int_{-\infty}^{\infty}d\sigma_1\int_{-\infty}^{\infty}d\sigma_2\cdots\int_{-\infty}^{\infty}d\sigma_n\\&\quad\times\exp\left[i\sum_{p=1}^{n}\{v\mu_p\sigma_p-\tfrac{1}{2}D^2\sigma_p^2\}\right]\\&=\frac{2^n}{n!}\left[\int_{-\infty}^{\infty}d\mu\int_{-\infty}^{\infty}d\sigma\,\exp(iv\mu\sigma-\tfrac{1}{2}D^2\sigma^2)\right]^n\\&=\frac{1}{2}\frac{1}{n!}\left(\frac{4\pi}{|v|}\right)^n.\end{aligned} \tag{44}$$

Inserting the above result into Eq. (20), we obtain

$$P=P_{\rm SD}\equiv\tfrac{1}{2}\{1-\exp(-4\pi J^2/|v|)\}. \tag{45}$$

This formula has been derived by one of the present authors[28] with a slightly different argument for the stochastic model. It should be noted that

$$P_{\rm SD}\to2\pi J^2/|v| \quad \text{for } J^2/|v|\to0, \tag{46}$$

as is consistent with the previous argument and

$$P_{\rm SD}\to\tfrac{1}{2} \quad \text{for } J^2/|v|\to\infty. \tag{47}$$

This means that the strong decoherence reduces the whole transition process to diffusionlike so that the system exists with even probability in both states after the slow passage.

Next we consider the effect of the energy dissipation for general values of ΔE. According to the pairing-off theorem and the lemma for the signature, we have

$$\begin{aligned}L^{(n)}&=2^{n-1}\int_{-\infty}^{\infty}d\mu_1\int_{\mu_1}^{\infty}d\mu_2\cdots\int_{\mu_{n-1}}^{\infty}d\mu_n\\&\quad\times\int_{-\infty}^{\infty}d\sigma_1\int_{-\infty}^{\infty}d\sigma_2\cdots\int_{-\infty}^{\infty}d\sigma_n\\&\quad\times\sum_c\exp\left[i\sum_{p=1}^{n}E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)\sigma_p\right.\\&\quad\left.-\tfrac{1}{2}D^2\sum_{p=1}^{n}\sigma_p^2\right],\end{aligned} \tag{48}$$

where the summation Σ_c runs over all of the possible configurations of the vertical pairs. The integration over σ_p gives

$$\begin{aligned}L^{(n)}&=2^{n-1}\int_{-\infty}^{\infty}d\mu_1\int_{\mu_1}^{\infty}d\mu_2\cdots\int_{\mu_{n-1}}^{\infty}d\mu_n\\&\quad\times\sum_c\prod_{p=1}^{n}K(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p),\end{aligned} \tag{49}$$

where

$$\begin{aligned}&K(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)\\&\quad=\frac{\sqrt{2\pi}}{D}\exp\left[-\frac{E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)^2}{2D^2}\right].\end{aligned} \tag{50}$$

Equation (49) indicates that the probability P is determined by the successive incoherent transitions of the wave packets of phonons, which are subject to sudden shift of the equilibrium position while undergoing the relaxed oscillation. In the case of slow-passage limit, we can approximate the Franck-Condon energy $E_p^{(q)}(\mu_{v_1},\mu_{v_2},\ldots,\mu_{v_q};\mu_p)$ by its asymptotic value $E_p^{(q)}\equiv v\mu_p+(-1)^{(q+1)}\Delta E$ for $|\mu_p-\mu_j|\gg\tau_{\rm en}$ since the variables μ_p are distributed sparsely in the integral domain of order of $\tau_{\rm tr}$. This means that the phonon system is relaxed to the equilibrium configuration immediately after the transition so that each transition event occurs always from the bottoms of the adiabatic potentials of the respective electronic subspace. The equilibrium configuration at time μ_p depends on the number q of the vertical pairs before μ_p. If we define the line-shape function $F_\pm(\mu)$ by

$$\begin{aligned}F_\pm(\mu)&=\int_{-\infty}^{\infty}\exp\left[-i(\Delta E\pm v\mu)\sigma-\frac{D^2}{2}\sigma^2\right]d\sigma\\&=\frac{\sqrt{2\pi}}{D}\exp[-(\Delta E\pm v\mu)^2/2D^2],\end{aligned} \tag{51}$$

the integrand of Eq. (49) is given as a sum of all the possible combinations of the terms like $F_-(\mu_1)F_-(\mu_2)F_+(\mu_3)\cdots F_+(\mu_n)$. Note that the first component is always $F_-(\mu_1)$. Again, an inspection leads to the following lemma.

Lemma 2. In the total set of possible diagrams that appear in the $2n$th-order terms of the perturbation expansion, all the combinations of $F_{j2}(\mu_2)F_{j3}(\mu_3)\cdots F_{jn}(\mu_n)$ with $j_p=\pm$ $(p=2,3,...,n)$ appear once.

Then $L^{(n)}$ is given by

$$L^{(n)}=\int_{-\infty}^{\infty}d\mu_1\int_{\mu_1}^{\infty}d\mu_2\cdots\int_{\mu_{n-1}}^{\infty}d\mu_n F_-(\mu_1)\times\prod_{m=2}^{n}\{F_+(\mu_m)+F_-(\mu_m)\}. \tag{52}$$

Since the integral is unchanged against the permutations of $(\mu_2,\mu_3,...,\mu_n)$, we have

$$L^{(n)}=\frac{1}{(n-1)!}\int_{-\infty}^{\infty}d\mu_1 F_-(\mu_1)\times\left[\int_{\mu_1}^{\infty}d\mu_2\{F_+(\mu_2)+F_-(\mu_2)\}\right]^{n-1}, \tag{53}$$

and, by inserting this into Eq. (20),

$$P=J^2\int_{-\infty}^{\infty}d\mu_1 F_-(\mu_1)\times\exp\left[-J^2\int_{\mu_1}^{\infty}d\mu_2\{F_+(\mu_2)+F_-(\mu_2)\}\right]. \tag{54}$$

This is a central result of this section.

In the case of weak coupling and high temperature, we may put $F_+(\mu)=F_-(\mu)\equiv F(\mu)$ with $F(\mu)=(\sqrt{2\pi}/D)\exp(-v^2\mu^2/2D^2)$ and find

$$P=J^2\int_{-\infty}^{\infty}d\mu_1 F(\mu_1)\exp\left[-2J^2\int_{\mu_1}^{\infty}d\mu_2 F(\mu_2)\right]=\tfrac{1}{2}\{1-\exp[-4\pi J^2/|v|]\}, \tag{55}$$

which recovers the formula (45). In deriving the above result, use is made of the identity

$$\exp\left[\int_a^b dt\ f(t)\right]=1+\int_a^b dt\ f(t)\exp\left[\int_t^b d\tau\ f(\tau)\right]. \tag{56}$$

In the limit of strong coupling at low temperature, we set $\Delta E\to S\overline{\omega}$ and $D\to\sqrt{S}\overline{\omega}$. It should be noted that $F_+(\mu)$ and $F_-(\mu)$ have nonvanishing values only at around $\mu=-\Delta E/v$ and $\mu=\Delta E/v$, respectively. The value of P strongly depends on the sign of v. We denote the value of P for $v>0$ $(v<0)$ as P_+ (P_-) hereafter. In the case $v>0$, $F_+(\mu)$ in the exponent of Eq. (54) can be neglected since the contribution from μ_1 integration is limited at around $\mu_1\simeq\Delta E/v$. Then, we have

$$P_+=J^2\int_{-\infty}^{\infty}d\mu_1 F_-(\mu_1)\exp\left[-J^2\int_{\mu_1}^{\infty}d\mu_2 F_-(\mu_2)\right]=1-\exp(-2\pi J^2/|v|)=P_{\rm LZ}. \tag{57}$$

On the other hand, in the case $v<0$, both $F_+(\mu)$ and $F_-(\mu)$ must be considered. By using the identity (56), Eq. (54) can be rewritten as

$$P=J^2\int_{-\infty}^{\infty}d\mu_1 F_-(\mu_1)\exp\left[-J^2\int_{\mu_1}^{\infty}d\mu_2 F_-(\mu_2)\right]\times\left\{1-J^2\int_{\mu_1}^{\infty}d\mu_3 F_+(\mu_3)\exp\left[-J^2\int_{\mu_3}^{\infty}d\mu_4 F_+(\mu_4)\right]\right\}. \tag{58}$$

Since the nonvanishing domains of $F_+(\mu)$ and $F_-(\mu)$ are separated far from each other and since the contribution of the integral over μ_1 comes from $\mu_1\simeq\Delta E/v\ll 0$, the lower limit of the integration over μ_3 can be safely extended to $-\infty$. Thus the integration over μ_1 and μ_3 can be decoupled and we find

$$P_-=\{1-\exp(-2\pi J^2/|v|)\}\exp(-2\pi J^2/|v|)=P_{\rm LZ}(1-P_{\rm LZ}). \tag{59}$$

Ao and Rammer[30] first pointed out that, at zero temperature, the transition rate becomes identical with the Landau-Zener formula in spite of the dissipation. This is correct provided that the speed of passage is slow enough and the crossing occurs from the lower-energy side. For intermediate values of v, P_+ deviates from $P_{\rm LZ}$ to increase the apparent nonadiabaticity, as will be shown in Sec. V. It is a little surprising that P_+ becomes identical with $P_{\rm LZ}$ both in the limit of rapid passage as shown in Eq. (40), and in the slow passage as shown in Eq. (57). The reason is, however, quite different between the two cases. Since the original Landau-Zener formula is derived for the coherent process, it may be said that the formula (57) obtained for the incoherent limit is a result of coincidence.[30] In the case $v<0$, the sequential application of $P_{\rm LZ}$ leads to Eq. (59) as a whole transition rate. The level crossing effectively occurs twice in this case, first at $t=-\Delta E/|v|$ and next at $t=\Delta E/|v|$ as shown in Fig. 3. If one notes that F_+ and F_- are interchanged by the change of the sign of v, a useful relation is obtained from Eq. (54) as

$$P_++P_-=J^2\int_{-\infty}^{\infty}d\mu_1\{F_+(\mu_1)+F_-(\mu_1)\}\times\exp\left[-J^2\int_{\mu_1}^{\infty}d\mu_2\{F_+(\mu_2)+F_-(\mu_2)\}\right]=1-\exp(-4\pi J^2/|v|)=2P_{\rm SD}, \tag{60}$$

which is generally valid in the limit of strong decoherence irrespective of the temperature.

Finally, we briefly discuss another extreme situation that is specified by Eq. (14), namely, the limit of the energy fluctuation alone. In this case, it is appropriate to treat the environmental perturbation as a Gaussian stochastic fluctuation of the energy levels with the amplitude D and the decay constant of the correlation of order of γ_p.[28] It has been shown that, as a function of the speed of the passage, there is an optimum value of v that maximizes the transition rate, and P tends to $\frac{1}{2}$ in the limit of slow passage. Generally, P is

bounded as $P_{\rm SD}\leqslant P\leqslant P_{\rm LZ}$ for a fixed value of $J^2/|v|$. In the limit of the large amplitude fluctuation, P agrees with $P_{\rm SD}$ as it should.

IV. INTERACTION MODE AND DAMPING OPERATOR

In order to see the overall features, we perform numerical calculations of the transition dynamics by using the damping operator technique. The damping operator is a hyperoperator operating on the density matrix and is widely utilized to describe the quantum damping of photon fields.[35] It was also applied to the calculation of the second-order optical spectrum of a localized electron-phonon system.[36] Recently, Murao and co-workers[37] developed an elegant formalism to solve the equation of motion for the density matrix with a damping term and carried out a numerical calculation of the transition dynamics of a level-crossing system. But the type of interaction considered by them is different from that treated here.

Since we are interested not only in the weak-coupling case with the phonons but also in the strong-coupling case, it is appropriate to separate out a part of the phonon degrees of freedom as the system mode and regard the rest as the reservoir modes. This can be achieved by introducing the *interaction mode*. The interaction mode was first proposed by Toyozawa and Inoue[38] for the Jahn-Teller system. In a little different form, it was also introduced by O'Brien.[39] The essential point of the interaction mode is that one can construct, out of a tremendous number of normal modes, a small number of modes that bear all of the relaxation energy within the relevant electronic subspace as components of the system. The rest of the modes span a basis set of the orthogonal complement of the interaction mode, which can be regarded as the reservoir R. In the present case, the annihilation operators B for the interaction mode and R_j for the reservoir modes are defined by the unitary transformation[39]

$$B=\sum_{k=1}^{N} U_{0,k}b_k, \tag{61}$$

$$R_j=\sum_{k=1}^{N} U_{j,k}b_k, \quad j=1,2,...,N-1. \tag{62}$$

The condition that the interaction mode carries all of the relaxation energy requires

$$U_{0,k}=\alpha_k/\alpha, \tag{63}$$

with $\alpha^2\equiv\Sigma_k\alpha_k^2(\equiv S)$. The transformation coefficients $U_{j,k}$ $(j=1,2,...,N-1)$ are defined so that R_j's lie in the orthogonal complement of B and are mutually orthogonal. Lagrange's method of indeterminate coefficients tells us that

$$U_{j,k}=\frac{\alpha_k}{(\omega_k-\Omega_j)c_j}, \quad j=1,2,...,N-1, \tag{64}$$

where $c_j^2\equiv\Sigma_k\alpha_k^2/(\omega_k-\Omega_j)^2$ and Ω_j is the frequency of the jth reservoir mode given by the root of the equation

$$\sum_k \frac{\alpha_k^2}{\omega_k-\Omega}=0. \tag{65}$$

The Hamiltonian (1) is then rewritten, in the matrix form, as

$$H(t)=H_{\rm sys}(t)+V_{\rm sys}+H_R+V_R, \tag{66}$$

$$H_{\rm sys}(t)=\begin{pmatrix} \frac{1}{2}vt+\overline{\omega}B_1^\dagger B_1 & 0 \\ 0 & -\frac{1}{2}vt+\overline{\omega}B_2^\dagger B_2 \end{pmatrix}, \tag{67}$$

$$V_{\rm sys}=\begin{pmatrix} 0 & J \\ J & 0 \end{pmatrix}, \tag{68}$$

$$H_R=\sum_j \Omega_j R_j^\dagger R_j \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{69}$$

$$V_R=\begin{pmatrix} \sum_j \beta_j(B_1^\dagger R_j+B_1R_j^\dagger) & 0 \\ 0 & \sum_j \beta_j(B_2^\dagger R_j+B_2R_j^\dagger) \end{pmatrix}, \tag{70}$$

where

$$B_1\equiv B+\frac{\alpha}{2}, \quad B_2\equiv B-\frac{\alpha}{2},$$

$\overline{\omega}$ is the frequency of the interaction mode given by

$$\overline{\omega}=\sum_k \omega_k U_{0,k}^2 \tag{71}$$

and β_j is the coupling constant between the interaction mode and the reservoir modes,

$$\beta_j=\sum_k \omega_k U_{j,k}U_{0,k}. \tag{72}$$

In the above equations, the (i,j) element represents $\langle i|H|j\rangle$. It should be noted that the above definition correctly guarantees the relaxation of the interaction mode to the lowest state within the respective electronic subspace. It can be shown that the concept of the interaction mode is extended in a unique way to generic n-level systems coupled linearly with boson fields. Details will be presented elsewhere.

The damping operator for the interaction mode coupled with the two-level system is introduced by extending the well-known procedure.[35] The equation of motion for the total density matrix in the interaction representation is solved for a short time interval by perturbation expansion to first order with respect to $V_{\rm sys}$ and to second order with respect to V_R. The variables for the reservoir modes are then eliminated by taking the trace over R. Under the assumption that the thermal equilibrium of R is undisturbed by the interaction and that the spectrum of R is wide enough to guarantee the Markovian approximation, we obtain the reduced equation of motion for the density matrix of the system. In the Schrödinger picture, it reads

$$i\frac{\partial}{\partial t}\tilde{\rho}=[H_{\rm sys}(t)+V_{\rm sys},\tilde{\rho}]+i\Gamma\tilde{\rho}, \tag{73}$$

in which Γ is a hyperoperator defined for the 2×2 density matrix

$$\tilde{\rho} \equiv \begin{pmatrix} \rho_{1,1} & \rho_{1,2} \\ \rho_{2,1} & \rho_{2,2} \end{pmatrix}, \tag{74}$$

as

$$\Gamma\tilde{\rho} = \begin{pmatrix} \Gamma_{1,1}\rho_{1,1} & \Gamma_{1,2}\rho_{1,2} \\ \Gamma_{2,1}\rho_{2,1} & \Gamma_{2,2}\rho_{2,2} \end{pmatrix}, \tag{75}$$

with

$$\Gamma_{i,j}\rho_{i,j} = \kappa(\bar{n}+1)(2B_i\rho_{i,j}B_j^\dagger - B_i^\dagger B_i\rho_{i,j} - \rho_{i,j}B_j^\dagger B_j) + \kappa\bar{n}(2B_i^\dagger\rho_{i,j}B_j - B_iB_i^\dagger\rho_{i,j} - \rho_{i,j}B_jB_j^\dagger). \tag{76}$$

In the above equation, κ is the effective coupling constant with the reservoir modes given by $\kappa \equiv \pi\bar{\beta}^2$ where $\bar{\beta}^2$ is the value of β_j^2 at $\Omega_j = \bar{\omega}$ multiplied by the density of state, and $\bar{n} \equiv 1/\{\exp[\bar{\omega}/k_BT] - 1\}$. The energy relaxation time $\tau_{\rm en}$ is given by $\tau_{\rm en} \simeq \kappa^{-1}$. We will treat κ as a free parameter, although the above equations are derived under rather restricted conditions on the spectrum of the reservoir modes and the coupling constant as well.

V. NUMERICAL RESULTS

Equation (73) is transformed into a simultaneous equation for the coefficients of the number state representation of the interaction mode and solved numerically. In the typical cases of high temperature, about 120 000 basis states are needed for the calculation. The probability $p(t)$ that the system exists in $|2\rangle$ at time t under the condition it starts from $|1\rangle$ at a remote past is calculated. The notations $p_+(t)$ and $p_-(t)$ are used in order to specify the sign of v; $p_+(t)$ for $v>0$ and $p_-(t)$ for $v<0$. In the presentation of the results, we adopt the dimensionless parameters normalized by $\bar{\omega}$; $\tilde{J} \equiv J/\bar{\omega}$, $\tilde{v} \equiv v/\bar{\omega}^2$, $\tilde{\kappa} \equiv \kappa/\bar{\omega}$, $\tilde{T} \equiv k_BT/\bar{\omega}$, and $\tilde{D} \equiv D/\bar{\omega}$.

First we show results for the low-temperature, strong-coupling limit. In Fig. 4, examples of the calculated $p_+(t)$ are given for fixed values of $S(=10)$, $\tilde{J}(=0.5)$, and $\tilde{\kappa}$ $(=0.2)$ at zero temperature with $\tilde{v}$ as a parameter. In Fig. 5 is also shown $p_-(t)$ for the same parameter values as in Fig. 4, but for the negative sign of v. The behaviors of $p_+(t)$ and $p_-(t)$ are very similar in the rapid passage case, $|\tilde{v}| = 25$, for example, and $P_+ \equiv \lim_{t\to\infty} p_+(t)$ and $P_- \equiv \lim_{t\to\infty} p_-(t)$ agree with the Landau-Zener formula, $P_+ = P_- = P_{\rm LZ}$, fairly well. This is the case of coherent transition given by Eq. (40). As $|\tilde{v}|$ becomes smaller, the difference between $p_+(t)$ and $p_-(t)$ becomes evident. The behavior of $p_-(t)$ clearly shows the back-transfer effect. One of the remarkable results is that in the case of slow passage, the relation $p_+(t) + p_-(t) = 1$ holds for $t \gtrsim 0$ for the same value of $|v|$, as can be seen from the comparison of the curves for $|\tilde{v}| = 0.25$. This means that the branching ratio to the upper and the lower state after the crossing does not depend on the initial condition whether the system starts from the upper branch or the lower, as if it forgets the history from which it came.

In order to see the dependence of the transition dynamics on the speed of passage, the values of P_+ (circle) and P_- (diamond) are plotted in Fig. 6 against $1/|\tilde{v}|$ for a fixed value of the adiabaticity parameter $J^2/|v|$ $(=0.2)$ at zero temperature with $S = 10.0$ and $\tilde{\kappa} = 0.2$. The values of $P_{\rm LZ}$ and $P_{\rm LZ}(1-P_{\rm LZ})$ are also shown in the figure. In the limit of rapid passage, $1/|\tilde{v}| \to 0$, the process becomes coherent so that $P_+ = P_- = P_{\rm LZ}$ as described earlier. As the speed of passage decreases, both P_+ and P_- deviates from $P_{\rm LZ}$ to lower values by the same amount. This increase of the nonadiabaticity is due to the phase relaxation. As $|v|$ decreases further, P_+ takes a minimum value at an intermediate value of $1/|v|$ and then increases again to approach to $P_{\rm LZ}$ in the limit of slow passage, consistently with formula (57). On the other hand, P_- decreases dramatically from $P_{\rm LZ}$ to $P_{\rm LZ}(1-P_{\rm LZ})$ as $|v|$ is decreased. The small discrepancies between the cal-

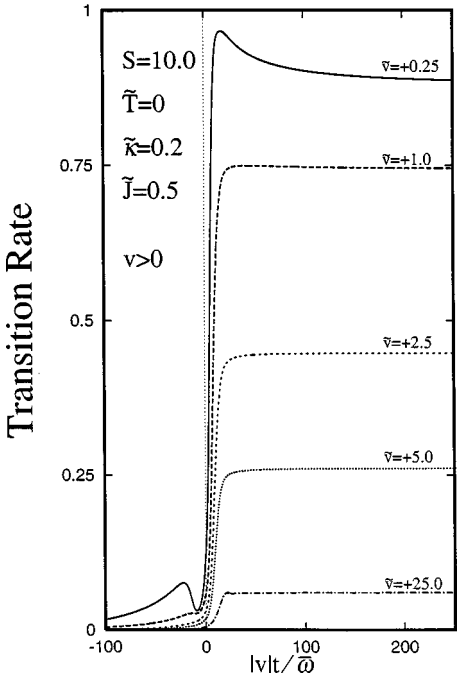

FIG. 4. The time-dependent probability $p_+(t)$ in the zero temperature, strong-coupling case with $v>0$ that the system exists in $|2\rangle$ for the initial condition that it starts from $|1\rangle$ at a remote past.

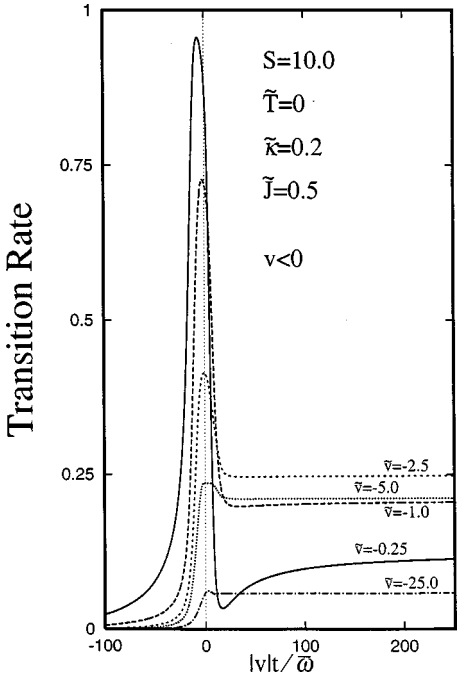

FIG. 5. The same as Fig. 4 for $p_-(t)$ where $v<0$.

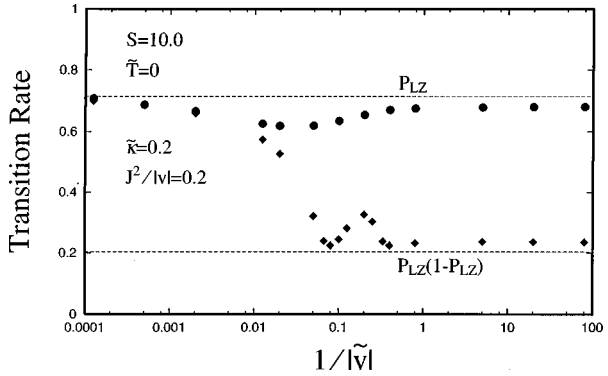

FIG. 6. The transition rate P_+ (circle) and P_- (diamond) as a function of $|\tilde{v}|^{-1}$ for a fixed value of $J^2/|v|$ in the zero-temperature, strong-coupling case. The predicted values by the formulas $P_{\rm LZ}$, and $P_{\rm LZ}(1-P_{\rm LZ})$ are shown by the dashed lines.

culated results and the prediction by formulas (57) and (59) in the limit $1/|\tilde{v}|\to\infty$ are due to the peculiar character of the damping operator and will be investigated later. We also note a dip in P_- as a function of $1/|\tilde{v}|$ at around $1/|\tilde{v}|\simeq 0.1$. This is interpreted as reflecting the dynamical motion of the wave packet in the configuration coordinate space of the interaction mode. The wave packet that has transferred to the potential curve of $|2\rangle$ at the first crossing shown in Fig. 3 undergoes a damping oscillation around the new equilibrium point. For $1/|\tilde{v}|\simeq 0.1$, the crossing point of the two potential curves moves down in synchronization with this motion so that the transfer rate form a dip at around $1/|\tilde{v}|\simeq 0.1$ because of the nearly adiabatic back transfer.

In Fig. 7, the transition rates P_+ and P_- are plotted for a fixed value of $\tilde{J}(=0.5)$ against $J^2/|v|$ with $\tilde{T}=0$, $S=10$, and $\tilde{\kappa}=0.2$. The value of $(P_++P_-)/2$ is also plotted by triangles. The values of $P_{\rm LZ}$, $P_{\rm LZ}(1-P_{\rm LZ})$, and $P_{\rm SD}$ are shown by dashed lines. For $J^2/|v|$ not greater than 0.5, P_+ and P_- agree with the formula $P_{\rm LZ}$ and $P_{\rm LZ}(1-P_{\rm LZ})$, respectively, fairly well. The discrepancy, which becomes salient for $J^2/|v|\gtrsim 0.5$ is again attributed to the special character of the damping operator. It is remarkable that the formula $(P_++P_-)/2=P_{\rm SD}$ given in Eq. (60) works quite well all through the parameter region.

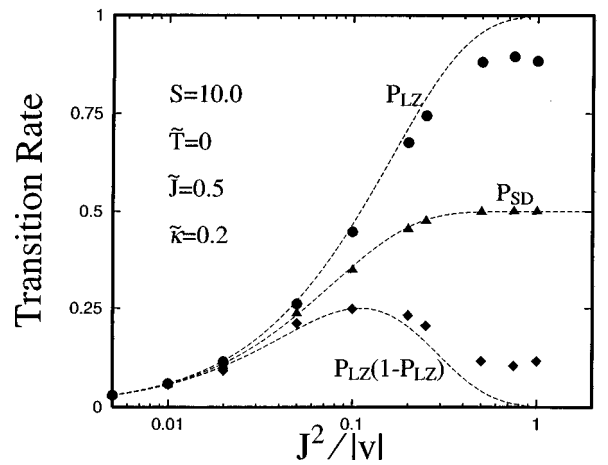

FIG. 7. The transition rate P_+ (circle) and P_- (diamond) as a function of $J^2/|v|$ in the zero-temperature, strong-coupling case for fixed values of $\tilde{\kappa}$, $\tilde{J}$, and S. The value of $(P_++P_-)/2$ is also plotted by the triangles. The prediction by the formulas $P_{\rm LZ}$, $P_{\rm LZ}(1-P_{\rm LZ})$, and $P_{\rm SD}$ are shown by the dashed lines.

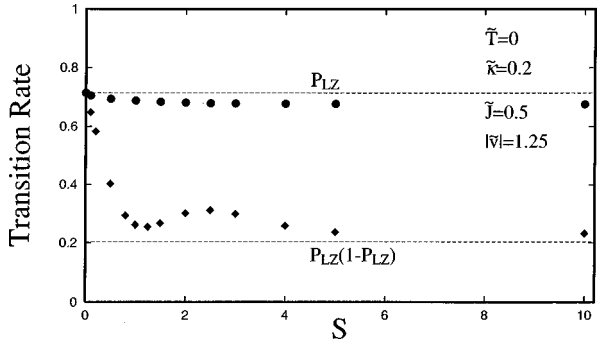

FIG. 8. The transition rate P_+ (circle) and P_- (diamond) as a function of S in the zero temperature, slow passage case for fixed values of $\tilde{J}$, $|v|$, and $\tilde{\kappa}$. The values of $P_{\rm LZ}$ and $P_{\rm LZ}(1-P_{\rm LZ})$ are given by the dashed lines.

The dependence on S of P_+ and P_- at zero temperature is shown in Fig. 8 for a fixed value of $\tilde{J}(=0.5)$ in the case of slow passage, $|\tilde{v}|=1.25$. It is remarkable that P_+ is essentially independent of S and is given by $P_{\rm LZ}$. On the contrary, P_- is reduced strongly by the coupling with phonons even in the weak-coupling region.

Now, we discuss the origin of the discrepancy between the formulas given in the previous section and the numerical results. It is essentially the difference in the short-time behavior of the correlation function between the original model given by Eqs. (1)–(4) and the reduced model given by Eqs. (73)–(76). In order to see this, we performed an analysis by the formal perturbation expansion series of the solution of Eq. (73) parallel to that given in Sec. III. The formal solution of Eq. (73) for the initial value $\tilde{\rho}_0$ is written as

$$\tilde{\rho}(t)=\mathrm{Exp}_+\left[-i\int_{-\infty}^{t}d\tau\,\mathcal{L}(\tau)\right]\tilde{\rho}_0, \tag{77}$$

with

$$\mathcal{L}(t)=\mathcal{L}_0(t)+\mathcal{L}', \tag{78}$$

where the hyperoperator $\mathcal{L}_0(t)$ and $\mathcal{L}'$ are defined by

$$\mathcal{L}_0(t)\tilde{\rho}=[H_{\rm sys}(t),\tilde{\rho}]+i\Gamma\tilde{\rho} \tag{79}$$

and

$$\mathcal{L}'\tilde{\rho}=[V_{\rm sys},\tilde{\rho}], \tag{80}$$

and $\mathrm{Exp}_+[\cdots]$ now represents the time-ordered exponential for the hyperoperators. By an analogous procedure given in Sec. III, $\rho(t)$ is expanded in a formal power series of $\mathcal{L}'$ as

$$\mathrm{Exp}_+\left[-i\int_{-\infty}^{t}d\tau\,\mathcal{L}(\tau)\right]\tilde{\rho}_0$$

$$=\mathrm{Exp}_+\left[-i\int_{-\infty}^{t}d\tau\,\mathcal{L}_0(\tau)\right]$$

$$\times\sum_{n=0}^{\infty}(-i)^n\int_{-\infty}^{t}d\tau_n\int_{-\infty}^{\tau_n}d\tau_{n-1}\cdots\int_{-\infty}^{\tau_2}d\tau_1$$

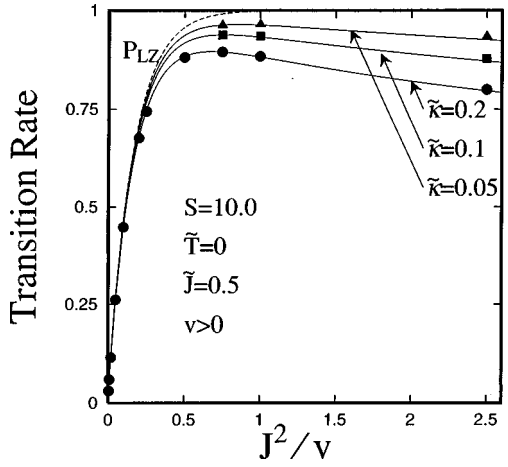

FIG. 9. The $\tilde{\kappa}$ dependence of P_+ as a function of $J^2/|v|$. The prediction by the formula (54) with replacement $F_\pm(\mu)\to\tilde{F}_\pm(\mu)$ is shown by the solid lines.

$$\times\mathcal{L}'(\tau_n)\mathcal{L}'(\tau_{n-1})\cdots\mathcal{L}'(\tau_1)\tilde{\rho}_0, \tag{81}$$

where $\mathcal{L}'(\tau)$ is the interaction representation of $\mathcal{L}'$. The expectation value of the above term is obtained after a somewhat complicated calculation by using the properties of the damping operator Γ. We arrive at the expression of the transition rate P,

$$P=-\sum_{n=1}^{\infty}(-J^2)^n\tilde{L}^{(n)} \tag{82}$$

where $\tilde{L}^{(n)}$ is given by the same form as given in Eq. (21) except that the function $G(t)$ is replaced by $\tilde{G}(t)$ given by

$$\tilde{G}(t)=-iS\bar{\omega}t+S(1-e^{-i\bar{\omega}t-\kappa|t|}), \tag{83}$$

at zero temperature. Note that $\tilde{G}(t)$ mimics the behavior of $G(t)$ fairly well but, in the limit $t\to 0$, it behaves as

$$\tilde{G}(t)\simeq S\kappa|t|+\frac{S}{2}(\bar{\omega}^2-\kappa^2)t^2, \tag{84}$$

for $S\gg 1$. This should be contrasted with the limiting value of $G(t)$,

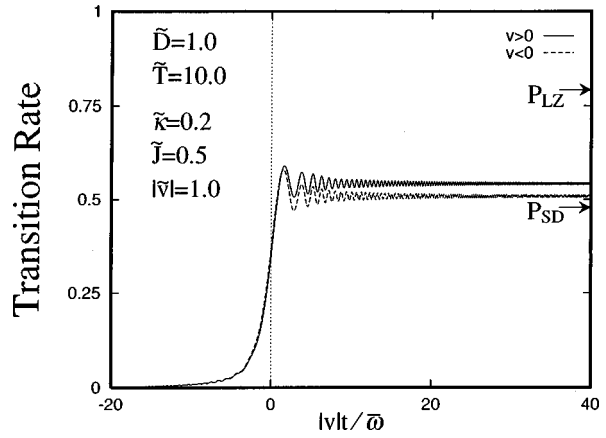

FIG. 10. The time-dependent probability $p_+(t)$ (solid line) and $p_-(t)$ (dashed line) in the case of high temperature, weak coupling.

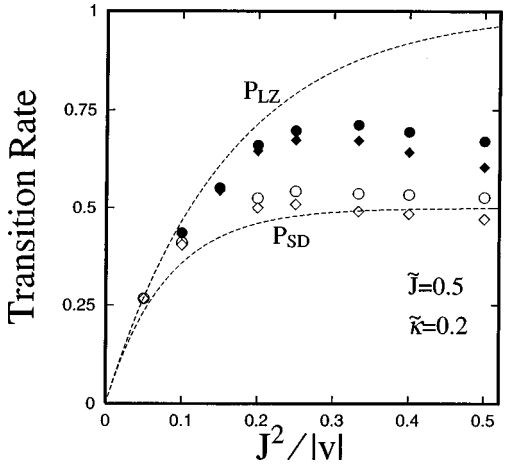

FIG. 11. The transition rate P_+ (circle) and P_- (diamond) in the case of high temperature, weak coupling. The results for $\tilde{D}=0.5$ and $\tilde{D}=1.0$ are shown by the solid and the open symbols, respectively.

$$G(t)\simeq\frac{S}{2}\bar{\omega}^2t^2. \tag{85}$$

Consequently, the line-shape function $\tilde{F}_\pm(\mu)$ becomes

$$\begin{aligned}\tilde{F}_\pm(\mu)&=\int d\sigma\ \exp[-i(\Delta E\pm v\mu)\sigma-\tilde{G}(\sigma)]\\&=\frac{1}{\pi}\frac{S\kappa}{\sqrt{2\pi}D^*}\int_{-\infty}^{\infty}dx\ \frac{1}{x^2+(S\kappa)^2}\\&\quad\times\exp\left[-\frac{(\Delta E\pm v\mu-x)^2}{2D^{*2}}\right]\end{aligned} \tag{86}$$

with $D^{*2}\equiv S(\bar{\omega}^2-\kappa^2)$, namely, the convolution of a Gaussian function with a Lorentzian function of width $S\kappa$. This is a consequence of the Markovian approximation assumed in the derivation of Eqs. (73)–(76). Since $\tilde{F}_\pm(\mu)$ has a Lorentzian tail for $|\mu\pm\Delta E/v|\gtrsim D^*/|v|$ unlike $F_\pm(\mu)$, the transition region is not confined well around the crossing times $\mu\simeq\pm\Delta E/|v|$. This off-resonant transition causes the derivation of P from the formulas. In fact, the hump before the steplike increase and the gradual decrease after it seen in Fig. 4 for the case $\tilde{v}=0.25$, for example, correspond to this effect. In order to ascertain this point, we have calculated P_+ as a function of $J^2/|v|$ for a number of parameter values of $\tilde{\kappa}$. In Fig. 9, the calculated results are shown with the value of formula (57) in which $F_-(\mu)$ is replaced by $\tilde{F}_-(\mu)$. The agreement is almost perfect. This analysis indicates that the simulation of the nonadiabatic processes by the damping operator technique is useful, but one must take care about the spurious effect peculiar to this method in the case of slow-passage limit.

Next, we turn to the high-temperature weak-coupling limit. In Fig. 10, an example of the numerical result is shown for $p_+(t)$ and $p_-(t)$ with parameter values $\tilde{T}=10.0$, $\tilde{D}=1.0$, $\tilde{J}=0.5$, $\tilde{\kappa}=0.2$, and $|\tilde{v}|=1.0$. In this case, the transition rate is almost independent of the sign of v and is strongly reduced from the value of P_{LZ}. In Fig. 11, the dependence on the adiabaticity parameter $J^2/|v|$ of P_+ and P_-

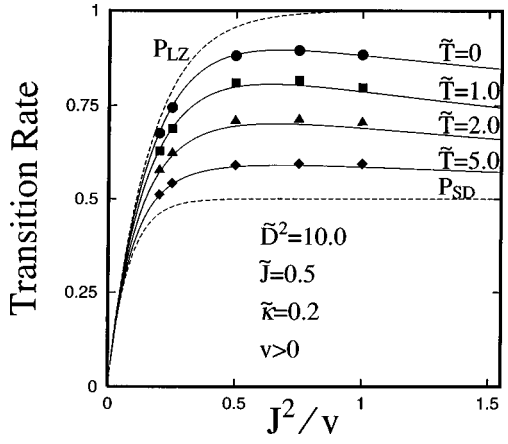

FIG. 12. The transition rate P_+ as a function of $J^2/|v|$ for the case of strong decoherence. The parameter $\tilde{D}$ is fixed as $\tilde{D}^2=10$ and the temperature $\tilde{T}$ is varied from 0 to 5 with corresponding change of S. The prediction by the formula (54) with the replacement $F_\pm(\mu)\to\tilde{F}_\pm(\mu)$ is shown by the solid lines.

is shown for the two parameter values of $\tilde{D}$ with other parameters fixed as $\tilde{J}=0.5$, $\tilde{\kappa}=0.2$. The coupling constant S and the temperature $\tilde{T}$ are chosen so that the condition (14) of the fluctuation dominance is satisfied; $S=0.0499$, $\tilde{T}=10.0$ for $\tilde{D}=1.0$ and $S=0.0249$, $\tilde{T}=5.0$ for $\tilde{D}=0.5$. This figure should be directly related with the results of the stochastic model.[28] As noted in Sec. III, P is generally bounded as $P_{\rm SD}\leqslant P\leqslant P_{\rm LZ}$ except for small deviations, takes a maximum value at an intermediate value of $|v|$ because of the tradeoff between the influence of the phase relaxation, which increases the nonadiabaticity, and the slowness of the passage, which favors the adiabaticity.[17] It is shown that P tends to $P_{\rm SD}$ in the limit $\tilde{D}\to\infty$.

Finally, in Fig. 12, we show numerical results of P_+ in the limit of large-amplitude fluctuation by changing the set of parameters $(S,\tilde{T})$ for the fixed value of $\tilde{D}^2\equiv S(2\bar{n}+1)$ $(=10)$ from the low-temperature, strong-coupling limit to the high-temperature, weak-coupling limit. The prediction of the general formula (54) with replacement $F_\pm(\mu)\to\tilde{F}_\pm(\mu)$ is shown by the solid curve. The agreement is good, which indicates the correctness of the analysis in Sec. III. The deviation from $P_+=P_{\rm LZ}$ in the limit $\tilde{T}=0$ is again due to the Lorentzian tail of the line-shape function. If the line-shape function $F_\pm(\mu)$ has only a Gaussian tail, P_+ should coincide with $P_{\rm LZ}$ in this limit. See how the functional form of the transition rate changes from $P_{\rm LZ}$ to $P_{\rm SD}$ as the temperature increases.

VI. CONCLUDING REMARKS

In this work, we have clarified the transition dynamics of a level-crossing system with dissipation both by analytical consideration and by numerical calculation. It has been shown that there are two extreme situations with respect to the ratio of the transition time $\tau_{\rm tr}$ and the phase relaxation time $\tau_{\rm ph}$, namely, the essentially coherent case with $\tau_{\rm tr}\ll\tau_{\rm ph}$ and the incoherent case with $\tau_{\rm tr}\gg\tau_{\rm ph}$. The latter case is further classified into two in accordance with the magnitude of the energy relaxation, the strong-coupling limit, and the weak-coupling high-temperature limit. A closed expression of the transition rate that covers the incoherent limit has been obtained. Numerical simulation of the time evolution of the two-level system has been carried out by applying the damping operator technique to the interaction mode.

It may be said that the Landau-Zener formula has a kind of *stability* against the dissipative perturbation. It is unaltered in the limit of rapid passage, or the slow modulation limit, as shown in Eq. (40). It is also valid to describe the transition rate in the limit of slow passage at low temperature, namely, the rapid modulation limit, as shown in Eq. (57). This stability is most clearly exhibited in Fig. 7. In the analysis of nonradiative hot transition at a potential curve crossing in a strongly coupled electron-phonon system, Sumi[9] concluded that the transition rate is given by the Landau-Zener formula under the condition that the wave packet of the phonon is relaxed from a higher state. This is correct, but his argument is constructed upon the assumption of strong decoherence, just the same as developed in the derivation of Eq. (57). The truth is that the Landau-Zener formula becomes applicable to this case because the wave packet passes the crossing region so rapidly that the modulation is in the slow limit[10] as described in the derivation of Eq. (40). It should be noted that, in this case, the condition of coherence is satisfied only for a time interval $\tau_{\rm tr}$ but may be broken in a longer time scale. This is the case classified into the short-range coherence.[21] The consideration about the degree of coherence over a long time scale is very important for the analysis of the dynamical processes involving repeated level crossing, since the phase coherence between the crossing levels plays an essential role in determining the successive transition rate.[20,21,23,40]

In the present model, the energies of the two electronic levels are assumed to be explicit functions of time, like the case of external modulation. This assumption is justified for the analysis of a single crossing event of dynamical systems if the degree of freedom, which modulates the electronic levels, is heavy enough. In actual situations, however, it may be that the reaction from the dissipative media modifies the motion of the heavy coordinate. Furthermore, we often encounter the cases where the electronic system is so strongly coupled with the dissipative media that the modulation of the energy itself is caused by this coupling. The strongly coupled localized electron-phonon system in solids mentioned above is a typical example. In order to analyze the experimental data of various dynamical phenomena of such systems, the whole process should be treated as an autonomous evolution. It is also required to develop an efficient and reliable technique of numerical calculation. A preliminary result of the analysis of the nonradiative hot transition in a localized center with potential curve crossing has been reported,[41] and its full account will be presented in a forthcoming paper.

ACKNOWLEDGMENTS

One of the authors (Y.K.) would like to express sincere thanks to Professor Y. Toyozawa for enlightening discussions in the early stage of this work. The other author (H.N.) would like to thank Professor H. Katayama-Yoshida for valuable discussions. A part of the numerical calculation was done by NEC SX-4 at the Computation Center, Osaka University. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

[1] See, for example, M. S. Child, *Molecular Collision Theory* (Academic, London, 1974); A. P. M. Baede, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, London, 1975), Vol. 30, p. 463.
[2] L. D. Landau, Phys. Z. Sowjetunion **1**, 88 (1932).
[3] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[4] See, for instance, C. Zhu and H. Nakamura, J. Chem. Phys. **101**, 10 630 (1994), and references therein.
[5] D. L. Dexter, C. C. Klick, and C. A. Russel, Phys. Rev. **110**, 603 (1955); R. Englman and B. Barnett, J. Lumin. **3**, 37 (1970); A. M. Stoneham, Rep. Prog. Phys. **44**, 1251 (1981).
[6] C. H. Henry and D. Lang, Phys. Rev. B **15**, 989 (1975).
[7] Y. Kayanuma and K. Nasu, Solid State Commun. **27**, 1371 (1978).
[8] M. Kusunoki, Phys. Rev. B **20**, 2512 (1979).
[9] H. Sumi, J. Phys. Soc. Jpn. **49**, 1701 (1980).
[10] Y. Kayanuma, J. Phys. Soc. Jpn. **51**, 3526 (1982).
[11] J. C. Tully, Phys. Rev. B **16**, 4323 (1977); J. Chem. Phys. **93**, 1061 (1990); W. Brenig, J. Phys. Soc. Jpn. **51**, 1914 (1982); H. Ueba, Phys. Rev. B **31**, 3915 (1985); S. Tsuneyuki and M. Tsukada, *ibid.* **34**, 5758 (1986); S. Sawada and M. Metiu, J. Chem. Phys. **84**, 6293 (1986).
[12] For example, R. D. Levine and R. Bernstein, *Molecular Reaction Dynamics* (Oxford University Press, Oxford, 1974); A. Nitzan and J. Jortner, J. Chem. Phys. **58**, 2412 (1973); H. Frauenfelder and P. Wolynes, Science **229**, 337 (1985); A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985); M. Sparpaglione and S. Mukamel, J. Phys. Chem. **91**, 3938 (1987).
[13] D. Glas and U. Mosel, Nucl. Phys. A **264**, 268 (1976); W. Nörenberg, Phys. Lett. **104B**, 107 (1981); B. Milek and R. Reif, *ibid.* **157B**, 134 (1985).
[14] A. A. Abragam, *The Principle of Nuclear Magnetism* (Oxford University Press, Oxford, 1975).
[15] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atom* (Wiley, New York, 1975); M. M. Roy, Phys. Rev. Lett. **32**, 814 (1974).
[16] C. Camparo and R. R. Frueholtz, Phys. Rev. A **30**, 803 (1984).
[17] Y. Kayanuma, Phys. Rev. Lett. **58**, 1934 (1987).
[18] S. Miyashita, J. Phys. Soc. Jpn. **64**, 3207 (1995).
[19] F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, Phys. Rev. Lett. **67**, 516 (1991); F. Grossmann and P. Hänggi, Europhys. Lett. **18**, 571 (1992).
[20] M. Morillo and R. I. Cukier, J. Chem. Phys. **98**, 4548 (1993).
[21] Y. Kayanuma, Phys. Rev. B **47**, 9940 (1993).
[22] M. Grifoni, M. Sassetti, J. Stockburger, and U. Weiss, Phys. Rev. E **48**, 3497 (1993).
[23] Y. Dakhonovskii, Phys. Rev. B **49**, 4649 (1994).
[24] Y. Kayanuma, J. Phys. Soc. Jpn. **54**, 2037 (1985).
[25] I. A. Goychuk, E. G. Petrov, and V. May, J. Chem. Phys. **103**, 4937 (1995).
[26] R. J. Spreeuw, N. J. van Druten, M. W. Beijersbergen, E. R. Eliel, and J. P. Woerden, Phys. Rev. Lett. **65**, 2642 (1990).
[27] M. Tsukada, J. Phys. Soc. Jpn. **51**, 2927 (1982).
[28] Y. Kayanuma, J. Phys. Soc. Jpn. **53**, 108 (1984); **53**, 118 (1984).
[29] Y. Gefen, E. Ben-Jacob, and A. O. Caldeira, Phys. Rev. B **36**, 2770 (1987).
[30] P. Ao and J. Rammer, Phys. Rev. B **43**, 5397 (1991).
[31] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981).
[32] S. Chakravarty and A. J. Leggett, Phys. Rev. Lett. **52**, 5 (1984); See also, H. Grabert and U. Weiss, *ibid.* **54**, 1605 (1985); M. P. A. Fisher and A. Dorsey, *ibid.* **54**, 1609 (1985).
[33] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[34] Y. Kayanuma, J. Phys. Soc. Jpn. **57**, 292 (1988); Phys. Rev. B **43**, 6326 (1991).
[35] See, for example, W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1989).
[36] T. Takagahara, E. Hanamura, and R. Kubo, J. Phys. Soc. Jpn. **44**, 728 (1978).
[37] M. Murao, C. Uchiyama, and F. Shibata, Physica A **209**, 444 (1994).
[38] Y. Toyozawa and M. Inoue, J. Phys. Soc. Jpn. **21**, 1663 (1966).
[39] M. C. M. O'Brien, J. Phys. C **5**, 2045 (1971).
[40] Y. Kayanuma, Phys. Rev. A **50**, 843 (1994); **55**, R2495 (1997).
[41] H. Nakayama, Y. Katayama-Yoshida, and Y. Kayanuma, in *Proceedings of the 23th International Conference on the Physics of Semiconductors, Berlin, 1996*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1997), p. 2817.