Quantum particle transfer in a system with a discontinuous modulation of the intersite coupling

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(Received 8 May 1996; revised manuscript received 31 July 1996)

The nonequilibrium density matrix technique is utilized to study the incoherent transfer of a quantum particle coupled to a fluctuating environment. The dynamics of the environment is assumed to split into two different types of molecular motions. The first type is associated with low-amplitude vibrations forming a thermal bath (TB). High-amplitude displacements of separated molecular groups define the second type and create stochastic fields for acting on the transferred particle. Specifying the TB by a set of harmonic oscillators and the stochastic fields by a dichotomic process averaged kinetic equations were derived. These equations enable us to construct a rate constants expressions and to find the steady-state populations for a quantum particle. Regimes of enhanced or reduced particle transfer are discussed in detail in relation to the characteristics of the stochastic field and the TB. [S1063-651X(96)07211-X]

PACS number(s): 02.50.Ey, 02.50.Wp, 05.20.Dd, 05.60.+w

I. INTRODUCTION

Transfer properties of a molecular system embedded in a condensed medium are determined by the interplay of dynamic and dissipative processes [1–10]. Concentrating on a local-state representation of a quantum particle moving in the molecular system under consideration the dynamic processes are characterized by the energy of the intrasite particle localization and the intersite coupling resulting in quantum jumps of the particle between neighboring sites. In contrast, the dissipative action of the environment can be attributed to several kinds of nuclear motions. These motions may differ significantly in their characteristic time scales and, therefore, may influence the particle transfer in different ways. First of all, one can set off from all possible motions the low-amplitude, nuclear vibrations forming a thermal bath (TB). Due to very fast relaxational processes with typical time constants τ_v in the order of $10^{-11}-10^{-13}$ s the vibrational states forming the TB are populated according to an equilibrium statistical distribution. Since the characteristic time scale of the transfer process Δt fulfills the inequality $\Delta t \gg \tau_v$, the TB can be described by an equilibrium density matrix.

Considering high-amplitude twisted and flipping motions of separate molecular groups or conformational fluctuations with the typical times $\tau_h \gg \tau_v$ this equilibrium description does not hold. For instance, one may find in proteins values of τ_h of $10^{-8}-10^{-10}$ s [11,12]. As a result, the rearrangement of these molecular groups creates stochastic fields which can be characterized by mean lifetimes τ_j (or mean escape frequencies $\nu_j = \tau_j^{-1}$) of the molecular groups related to the mean time they spent in the certain sites j. Remembering the inequality $\tau_v \ll \Delta t \sim \tau_h$ introduced for the transfer processes of interest the environment has to be simulated by the TB and the stochastic fields, but not by the stochastic fields alone.

To study systems where such a combined influence of a stochastic field and a TB has to be considered the method of the nonequilibrium density matrix (NDM) is utilized [13–21]. Redfield [22] and Bloch [23] were apparently the first who tried to derive a generalized kinetic equation (GKE) for the description of quantum transitions in a two-level system (TLS) interacting with a TB and a time-dependent field. A generalization of the Redfield-Bloch approach to the case of discontinuous stochastic fields was advocated by Burstein, Zharikov, and Temkin [24] and others [25–27] in a semiphenomenological way. An attempt to take into account, in an exact manner, the influence of the environment was undertaken in different papers (to mention a few we refer on Refs. [25–28]). In these papers, the environment was only considered by a time-dependent random field.

The correct treatment of dissipative processes is based on the *ensemble averaging* with respect to the equilibrium states of the TB. Such a scheme was often used in combination with the Born approximation [29–31], either for a weak system-TB interaction or for the case of strong coupling, i.e., in the so–called noninteracting blip approximation (NIBA) [10,32–34]. In the present paper we generalize the scheme of the ensemble averaging taking into account the stochastic processes.

The paper is organized as follows. In Sec.II the general treatment is presented including the derivation of the exact averaged GKE. The solution of the GKE describing a TLS under the action of a stochastic field is explained in Sec. III. Section IV deals with the simultaneous incorporation of a stochastic field and a TB. The paper ends with a discussion of the influence of the equilibrium and nonequilibrium part of an environment on the transfer of a quantum particle (Sec.V).

II. KINETIC EQUATIONS FOR THE AVERAGED DENSITY MATRIX OF A QUANTUM SYSTEM

To derive the GKE valid for the averaged NDM,

$$\sigma(t) = \overline{\rho(t)} \equiv \overline{\mathrm{Tr}_B \rho_{SB}(t)}, \tag{1}$$

where ρ_{SB} is the NDM of the quantum system plus the TB; the trace operation $\overline{\mathrm{Tr}_B}$ has to be carried out with respect to the TB states, and $\overline{O}$ denotes the averaging O with respect to the stochastic fields; we divide the total Hamiltonian $H(t)$ into three parts

$$H(t)=H_S(t)+H_B+V. \tag{2}$$

The first part

$$H_S(t)=H_0+H_f(t), \tag{3}$$

consists of the Hamiltonian of the quantum system of interest (the main dynamic part) H_0 and the part $H_f(t)$ including the action of the stochastic fields. The Hamiltonian of the TB, H_B, describes the vibrational states of the environment. In the harmonic approximation it reads

$$H_B=\sum_l \hbar\omega_l(b_l^+b_l+1/2), \tag{4}$$

where ω_l is the frequency of the lth bath mode and, $b_l^+(b_l)$ denote the respective creation (annihilation) operators. Introducing an expansion in the localized states $|n\rangle$ we get for the system Hamiltonian H_0 and the system-TB interaction V the following general form [7,21,29–32]:

$$H_0=\sum_{m,n} H_{m,n}|m\rangle\langle n|, \quad V=\sum_{nn'} \hat{F}_{nn'}|n\rangle\langle n'|. \tag{5}$$

Here, $\hat{F}_{nn'}$ is the operator of generalized force introduced by the TB.

A. Averaged forms of the GKE

Starting with the Liouville equation

$$i\dot{\rho}_{SB}(t)=L(t)\rho_{SB}(t), \tag{6}$$

where $L(t)\equiv\hbar^{-1}[H(t),\ldots]$, and the initial factorization $\rho_{SB}(0)=\rho(0)\rho_B$ where

$$\rho_B=\exp(-H_B/k_BT)/\mathrm{Tr}_B\exp(-H_B/k_BT) \tag{7}$$

is the TB equilibrium density matrix, in accord with definition (1), one obtains the following *exact* form of the desired NDM:

$$\sigma(t)=S_D(t,0)S_R(t,0)\rho(0). \tag{8}$$

Here, the pure dynamic and the averaged relaxation matrixes read

$$S_D(t,t')=\hat{T}\exp\left\{-i\int_{t'}^{t}L_D(\tau)d\tau\right\},$$
$$L_D(t)\equiv\hbar^{-1}[H_D(t),\ldots], \tag{9}$$

and

$$S_R(t,t')=\overline{\mathrm{Tr}_B\exp\{-iL_B(t-t')\}\hat{T}\exp\left\{-i\int_{t'}^{t}L_i^{\tau}(\tau)d\tau\right\}\rho_B}, \tag{10}$$

respectively. In Eqs. (9), (10) $\hat{T}$ denotes Dyson's chronological operator, and

$$L_i^t(t)=S_D^{-1}(t,0)e^{iL_Bt}L_i(t)e^{-iL_Bt}S_D(t,0),$$
$$L_i(t)\equiv\hbar^{-1}[H_i(t),\ldots], \quad L_B\equiv\hbar^{-1}[H_B,\ldots]. \tag{11}$$

Equation (8) splits the evolution of the NDM into a part of the averaged dynamic behavior [via the averaged Hamiltonian $H_D(t)\equiv\overline{H_S(t)}+\langle V\rangle_B$], and into the part of the averaged relaxational behavior [via the averaged deviations $H_i(t)\equiv H_f(t)-\overline{H_f(t)}+V-\langle V\rangle_B$ where $\langle V\rangle_B=\mathrm{Tr}_B\rho_BV$].

For the practical calculations, one needs the appropriate expansion procedure with respect to the deviations $H_i(t)$. It is possible to show from the exact form (8) that in the important case of the Born approximation, the averaged matrix $\sigma(t)$ can be found from the following integro–differential master equation

$$\dot{\sigma}(t)=-iL_D(t)\sigma(t)-\int_0^t K_0(t,t')\sigma(t')dt', \tag{12}$$

where the kernel

$$K_0(t,t')=\overline{\mathrm{Tr}_B[L_i(t)S_D(t,t')\exp\{-iL_B(t-t')\}L_i(t')\rho_B]} \tag{13}$$

can be calculated if one specifies the averaging procedure valid for the stochastic process under consideration.

The form (12) of a GKE is appropriate for the description of quantum systems when the reverse damping time τ_d^{-1} of the kernel (13) or the energy-level differences Δ exceed modulations caused by the stochastic field and the TB. It should be underlined that Eq. (12) is valid for any relation between the amplitudes and frequencies of the discontinuous stochastic field.

B. The stochastic form of the GKE

At strong stochastic field one must find a GKE which goes beyond the second order with respect to the deviation $H_f(t)-\overline{H_f(t)}$. Using the approach given in Refs. [15,19,29] and introducing the Born approximation with respect to $\Delta V=V-\langle V\rangle_B$ one obtains

$$\dot{\rho}(t)=-iL_S(t)\rho(t)-\int_0^t\Gamma(t,t')\rho(t')dt'. \tag{14}$$

Here, the density matrix of a quantum system $\rho(t)$, as well as the superoperator $L_S(t)\equiv\hbar^{-1}[(H_S(t)+\langle V\rangle_B),\ldots]$ and the relaxation matrix

$$\Gamma(t,t')=\mathrm{Tr}_B[L_VS(t,t')L_V\rho_B], \quad (L_V\equiv\hbar^{-1}[\Delta V,\ldots]), \tag{15}$$

are random operator functionals. The evolution matrix

$$S(t,t')=S_0(t,t')\exp\{-iL_B(t-t')\} \tag{16}$$

of Eq. (15) is expressed through the random dynamic matrix

$$S_0(t,t')=\hat{T}\exp\left\{-i\int_{t'}^{t}L_S(\tau)d\tau\right\}. \quad (17)$$

In contrast to the GKE (12) for the averaged NDM $\sigma(t)=\overline{\rho(t)}$, the approximate master equation (14) represents a stochastic GKE for a nonaveraged NDM $\rho(t)$ where, however, the stochastic field is taken into consideration in an exact manner. (For equations like Eq. (14) the averaging procedure has been discussed in a number of papers, see Refs. [25,28–30,32,35]).

Despite non-Markovian properties of Eq. (14) non-Markovian contributions only become of some importance if one introduces higher-order approximations with respect to ΔV (see, for instance, Refs. [19,21,29,36]). Practically, the approximation $\rho(t')\approx\rho(t)$ is valid if the characteristic time τ_d of the kernel $\Gamma(t,t')$ in Eq. (14) satisfies the inequality $\tau_d\ll\tau_r$ [37]. Here, τ_r determines the time scale of the relaxation behavior of $\rho(t)$ initiated by the interaction V. This statement has been proven by Oppenheim *et al.* [38] for a TLS interacting with a TB. If ζ denotes the effective coupling constant between the TB and the quantum system, $\Gamma(t,t')$ is proportional to ζ^2. Consequently, we get $\tau_r^{-1}\sim\zeta^2\tau_d$, and the Markov approximation is valid for $(\zeta\tau_d)^2\ll 1$. The inequality $(\zeta\tau_d)^2\ll 1$ simultaneously characterizes the applicability of the Markov and the Born approximation only if the characteristic time τ_0 of the pure dynamic processes exceeds τ_d. If Δ is a typical energy difference in the considered quantum system (or as the frequency of an external field) we may write $\tau_0\sim\Delta^{-1}$, and the condition $\tau_d\Delta\ll 1$ must also be valid. If $\tau_d\Delta\gg 1$ the Born approximation is correct because of $\Delta\gg\tau_r^{-1}$, but the applicability of the Markov approximation is questionable. Nevertheless, one can apply the Markov approximation to the GKE already averaged on the time scale $\Delta t\sim\Delta^{-1}$ of a fast dynamic process. For the example of a transfer process in the TLS all quantities ζ,τ_d,Δ will be specified in Sec. IV.

To proceed further we change to a representation of the GKE (14) in the localized state $|n\rangle$. In the tetradic representation the GKE reads

$$\dot{\rho}_{mn}(t)=-i\sum_{m'n'}\left\{L_{mn;m'n'}(t)\rho_{m'n'}(t)-\int_0^t\Gamma_{mn;m'n'}(t,t')\rho_{m'n'}(t')dt'\right\}, \quad (18)$$

where the stochastic dynamic and relaxation matrices are given by their matrix elements

$$L_{mn;m'n'}(t)=\frac{1}{\hbar}\{[H_S(t)+\langle V\rangle_B]_{mm'}\delta_{n'n}-[H_S(t)+\langle V\rangle_B]_{n'n}\delta_{mm'}\} \quad (19)$$

and

$$\begin{aligned}\Gamma_{mn;m'n'}(t,t')=\frac{1}{\hbar^2}\Sigma_{rr'}\{&K_{mr;r'm'}(t-t')S_{rn;r'n'}(t,t')\\&+K_{n'r';rn}[-(t-t')]S_{mr;m'r'}(t,t')\\&-K_{rn;r'm'}(t-t')S_{mr;r'n'}(t,t')\\&-K_{n'r';mr}[-(t-t')]S_{rn;m'r'}(t,t')\},\end{aligned} \quad (20)$$

respectively. The correlation function

$$K_{ab;a'b'}(t-t')=\langle\Delta\hat{F}_{ab}\Delta\hat{F}^{t-t'}_{a'b'}\rangle_B \quad (21)$$

of the force fluctuations $\Delta\hat{F}_{ab}=\hat{F}_{ab}-\langle\hat{F}_{ab}\rangle_B$ with $\Delta\hat{F}^t_{ab}=\exp(-iL_Bt)\Delta\hat{F}_{ab}$ determines the action of the TB on the relaxation process in a quantum system whereas the dynamic corrections of the relaxation process are defined by the stochastic matrix elements

$$S_{ab;a'b'}(t,t')=\langle a|S_0(t,t')\hat{\gamma}_{a'b'}|b\rangle. \quad (22)$$

This fact demonstrates the complex behavior of relaxation processes in a quantum system interacting simultaneously with a TB and a stochastic field.

To average Eq. (14) [or its tetradic form (18)] one has to specify both the stochastic process and the quantum system. In the problem under consideration we choose the discontinuous Markovian kangaroo process (KP) [24,25,29,39]. To specify a transfer process one has to note that it consists of elementary jumps between different sites of particle localization. Therefore, we will concentrate in the remaining part of the paper on a detailed investigation of particle transitions in a TLS.

III. RESTRICTION ON THE INFLUENCE OF THE STOCHASTIC FIELD

Neglecting the coupling to the TB we have $\Gamma(t,t')=0$. The formal solution of Eq. (14) for the noise averaged NDM follows as

$$\sigma(t)=\sigma_0(t)=\overline{S_0(t,0)}\rho(0), \quad (23)$$

where the stochastic field will be specified to a nonsymmetric dichotomous one. The remaining problem concerns the correct averaging of the dynamic matrix $S_0(t,0)$.

It is necessary to note here that in the standard treatment one finds the quantity $\sigma(t)=\overline{\rho(t)}$ by averaging Eq. (14) for the special case $\Gamma(t,t')=0$ (see details, for instance, in papers [28–30,32] and especially [40]). Unfortunately, this procedure only yields an exact result for a symmetric dichotomous process. For the case of a nonsymmetric dichotomous process one can use a technique proposed by Brissaud and Frish [39]. Below we will follow this approach.

A. General form of the averaged NDM

Let $R(t)\equiv\overline{S_0(t,0)}$. Since the stochastic matrix (17) obeys the necessary condition introduced in the approach of Brissaud and Frish, the matrix $R(t)$ can be found from its Laplace transform

$$\widetilde{R}(p)=\overline{A(p)}+\overline{\nu A(p)}[\overline{\nu I}-\overline{\nu^2 A(p)}]^{-1}\overline{\nu A(p)}. \quad (24)$$

For the dichotomous process under consideration we have

$$\overline{\nu^l A(p)}=\sum_{j=1}^{2} W_j \frac{\nu_j^l}{(p+\nu_j)I+iL_j}, \quad (L_j \equiv \hbar^{-1}[H_j, \ldots]),$$

$$\overline{\nu}=\sum_{j=1}^{2} W_j \nu_j = 2\nu_1\nu_2/(\nu_1+\nu_2), \quad (25)$$

where the probabilities $W_{1,2}=\nu_{2,1}/(\nu_1+\nu_2)$ are given by the escape frequencies ν_1, ν_2. The Hamiltonian H_j ($j=1,2$) is the possible realization of the TLS Hamiltonian

$$H_S(t)=\sum_{n=1,2} E_n|n\rangle\langle n|+\hbar\lambda(t)(|1\rangle\langle 2|+|2\rangle\langle 1|) \quad (26)$$

if the fluctuating intersite coupling strength $\lambda(t)$ is replaced by its realizations λ_1 and λ_2. Using the representation $|\mu\rangle=|\pm\rangle$ where

$$H_j=\sum_{\mu\mu'} H_{\mu\mu'}^{(i)}|\mu\rangle\langle\mu'|,$$

$$H_{++}^{(j)}=\varepsilon_1^{(j)}\cos^2\varphi_j+\varepsilon_2^{(j)}\sin^2\varphi_j,$$

$$H_{--}^{(j)}=\varepsilon_1^{(j)}\sin^2\varphi_j+\varepsilon_2^{(j)}\cos^2\varphi_j, \quad (27)$$

$$H_{+-}^{(j)}=H_{-+}^{(j)}=-\tfrac{1}{2}\hbar\Delta_j\sin 2\varphi_j,$$

and $\varphi_j=-(-1)^j\varphi$, $\varphi=(\chi_1-\chi_2)/2$,

$$\varepsilon_\alpha^{(j)}=\frac{1}{2}[E_1+E_2-(-1)^\alpha\hbar\Delta_j], \quad \Delta_j=\sqrt{\omega_0^2+4\lambda_j^2},$$

$$(\hbar\omega_0\equiv E_1-E_2\geqslant 0), \quad (28)$$

$$\tan\chi_j=\hbar|\lambda_j|/(\varepsilon_1{}^{(j)}-E_2), \quad (29)$$

one can derive the following expression for the averaged matrix (25)

$$\overline{\nu^l A(p)}=\begin{pmatrix} z_l & a_l & b_l & c_l \\ a_l & u_l & c_l & -a_l \\ b_l & c_l & w_l & -b_l \\ c_l & -a_l & -b_l & z_l \end{pmatrix}. \quad (30)$$

The various matrix elements read

$$z_l=\sum_j W_j\nu_j^l\alpha_j, \quad a_l=\sum_j W_j\nu_j^l\beta_j, \quad b_l=\sum_j W_j\nu_j^l\widetilde{\beta}_j,$$

$$c_l=\sum_j W_j\nu_j^l\gamma_j, \quad u_l=\sum_j W_j\nu_j^l\delta_j, \quad w_l=\sum_j W_j\nu_j^l\widetilde{\delta}_j, \quad (31)$$

where the following shortenings have been introduced:

$$\alpha_j=D_j^{-1}[(p+\nu_j)^2+f_j^2+2g_j^2],$$

$$\beta_j=-iD_j^{-1}g_j(p+\nu_j-if_j),$$

$$\gamma_j=2D_j^{-1}g_j^2, \quad \delta_j=D_j^{-1}[(p+\nu_j)(p+\nu_j-if_j)+2g_j^2], \quad (32)$$

$$D_j=(p+\nu_j)[(p+\nu_j)^2+\Delta_j^2].$$

The quantities $\widetilde{\beta}_j$ and $\widetilde{\delta}_j$ are obtained from β_j and δ_j, respectively, in substituting $-i$ by i. (Note, that the conditions $\widetilde{\beta}=\beta^*$ and $\widetilde{\delta}=\delta^*$ are not fulfilled since p is a complex quantity). In Eq. (32) the quantities

$$g_j=\tfrac{1}{2}\Delta_j\sin 2\varphi_j, \quad f_j=\Delta_j\cos 2\varphi_j \quad (33)$$

determine the pecularities of the stochastic process via the relations between realizations λ_j of the intersite random coupling $\lambda(t)$ and the specific frequency $\omega_0\equiv(E_1-E_2)/\hbar$. Equations (24), (30), (31), (32), and (33) specify the exact expression for the Laplace transform $\widetilde{R}(p)$ of the desired matrix $R(t)$ itself. A detailed inspection shows that each matrix element of $\widetilde{R}(p)$ is defined as a proper rational fraction and, in addition, the denominator's roots p_j of these matrix elements are given as simple roots. As a result, the time behavior of $R(t)$ is determined by a sum of terms containing multipliers $\exp(p_j t)$.

Below we specify the evolution processes in a TLS to the case of degenerated levels, i.e., $\omega_0=0$, and to the strongly nondegenerated case $\omega_0\gg|\lambda_j|$.

B. The case of the degenerated TLS

In accordance with Eqs. (28) and (29), at $\omega_0=0$ and $\lambda_j\geqslant 0$ we obtain $\chi_j=\pi/4$ and $\varphi_j=0$ for both realizations, λ_1 and λ_2, of the intersite coupling strength $\lambda(t)$. Since $\gamma_j=0$, $\beta_j=0$ the matrix (30) is reduced to the simple form with the following nonvanishing elements:

$$\widetilde{R}_{++;++}(p)=\widetilde{R}_{--;--}(p)=\frac{1}{p},$$

$$\widetilde{R}_{+-;+-}(p)=\frac{1}{\nu_1+\nu_2}\frac{2p(\nu_1+\nu_2)+(\nu_1+\nu_2)^2+4i(\nu_1\lambda_1+\nu_2\lambda_2)}{(p+2i\lambda_1)(p+\nu_2+2i\lambda_2)+(p+2i\lambda_2)(p+\nu_1+2i\lambda_1)}. \quad (34)$$

[$\widetilde{R}_{-+;-+}(p)$ follows from $\widetilde{R}_{+-;+-}(p)$ in substituting i by $-i$]. From Eq. (34) one finds immediately the poles $p_0=0$ and $p_{1,2}=-\gamma_{\pm}-i\Omega_{\pm}$ of the matrix $\widetilde{R}(p)$ and, thus, the analytic form of the matrix $R(t)$. The damping factors $\gamma_{\pm}$ as well as the effective frequencies $\Omega_{\pm}$ given by the expressions

$$\gamma_{\pm}=\frac{1}{2}\left(\nu\pm\sqrt{r}\cos\frac{\alpha}{2}\right),$$

$$\Omega_{\pm}=(\lambda_1+\lambda_2)\pm\frac{1}{2}\sqrt{r}\sin\frac{\alpha}{2}, \tag{35}$$

where the quantities

$$r=\sqrt{[\nu^2-4(\lambda_1-\lambda_2)^2]^2+4(\nu_1-\nu_2)^2(\lambda_1-\lambda_2)^2},$$

$$\nu=\frac{1}{2}(\nu_1+\nu_2), \tag{36}$$

$$\tan\alpha=\frac{2(\nu_1-\nu_2)(\lambda_1-\lambda_2)}{|\nu^2-4(\lambda_1-\lambda_2)^2|}$$

reflect the dependence of the transfer process on the amplitudes λ_1,λ_2 as well as frequencies ν_1,ν_2 of the discontinuous stochastic field. Expressions (35) are valid for $\nu^2\geqslant 4(\lambda_1-\lambda_2)^2$ and $\pi/2\geqslant\alpha\geqslant 0$. If $\nu^2\leqslant 4(\lambda_1-\lambda_2)^2$, one has to substitute α by $\pi-\alpha$ (we choose $\nu_1\geqslant\nu_2,\ \lambda_1-\lambda_2>0$).

Let the particle stay at site 1 for $t=0$. With the reverse Laplace transform and Eqs. (34), (35) we may derive the following expressions for the level populations $N_a(t)\equiv\sigma_{aa}(t)$. In the basis of the states $|\mu\rangle=|\pm\rangle$, one finds

$$N_+(t)=\tfrac{1}{2}R_{++;++}(t)=\tfrac{1}{2},\quad N_-(t)=\tfrac{1}{2}R_{--;--}(t)=\tfrac{1}{2}. \tag{37}$$

Alternatively, in the basis of localized states $|n\rangle$ we have

$$\begin{aligned}N_1(t)&=\tfrac{1}{4}[R_{++;++}(t)+R_{--;--}(t)+R_{+-;+-}(t)+R_{-+;-+}(t)]\\&=\frac{1}{2}+\frac{1}{8(\nu_1+\nu_2)\sqrt{r}}\Bigg\{e^{-\gamma_-t}\Bigg[\left((\nu_1+\nu_2)^2+2(\nu_1+\nu_2)\sqrt{r}\cos\frac{\alpha}{2}\right)\cos\left(\Omega_-t+\frac{\alpha}{2}\right)\\&\quad+2\left(2(\nu_1-\nu_2)(\lambda_1-\lambda_2)+(\nu_1+\nu_2)\sqrt{r}\sin\frac{\alpha}{2}\right)\sin\left(\Omega_-t+\frac{\alpha}{2}\right)\Bigg]-e^{-\gamma_+t}\Bigg[\left((\nu_1+\nu_2)^2-2(\nu_1+\nu_2)\sqrt{r}\cos\frac{\alpha}{2}\right)\\&\quad\times\cos\left(\Omega_+t+\frac{\alpha}{2}\right)+2\left(2(\nu_1-\nu_2)(\lambda_1-\lambda_2)-(\nu_1+\nu_2)\sqrt{r}\sin\frac{\alpha}{2}\right)\sin\left(\Omega_+t+\frac{\alpha}{2}\right)\Bigg]\Bigg\},\quad N_2(t)=1-N_1(t).\end{aligned} \tag{38}$$

In Fig. 1, the typical picture of the evolution process in a TLS is given for the case $\nu^2<4(\lambda_1-\lambda_2)^2$. One clearly observes the difference between the symmetric ($\nu_1=\nu_2$) and the asymmetric ($\nu_1\neq\nu_2$) influence of the dichotomous stochastic field. In particular, this asymmetry of the stochastic process generally favors the coherent character of the particle transfer in the TLS.

C. The case of the strongly nondegenerated TLS

Providing the inequality $\omega_0\gg\lambda_j$, the energy levels $\varepsilon_1^{(j)}$ and $\varepsilon_2^{(j)}$ of the delocalized states [see Eq. (28)] are nearly identical with the levels E_1 and E_2 of the localized states. In accordance with Eq. (29) it follows $\chi_j\approx 0$. Therefore, the quantities $\sin\varphi_j$ in Eqs. (31)–(33) can be used as small expansion parameters. As an example, we present analytic results being valid at $\nu_j<\omega_0$ and at any relations between the frequencies ν_1,ν_2 and the intersite couplings λ_1,λ_2, i.e., at any value of the respective Kubo number [37,40,41]. According to this expansion procedure we get

$$N_+(t)\approx N_1(t)\approx 1/2+[\rho_{11}(0)-1/2]\exp\{-k_{\parallel}t\}, \tag{39}$$

$$\sigma_{+-}(t)\approx\sigma_{12}(t)\approx\rho_{12}(0)\exp\{-i\omega_0 t\}\exp\{-k_{\perp}t\}, \tag{40}$$

$$\sigma_{-+}(t)=[\sigma_{+-}(t)]^*.$$

Here, the longitudinal and transverse rate constants $k_{\parallel}$ and $k_{\perp}$, respectively, are expressed by the root mean-square deviation σ_λ^2, as

$$k_{\parallel}=2k_{\perp}=\frac{4\sigma_\lambda^2\nu}{\nu^2+\omega_0^2},\quad\left(\sigma_\lambda^2\equiv\frac{\nu_1\nu_2(\lambda_1-\lambda_2)^2}{4\nu^2}\right). \tag{41}$$

Similar expressions had been derived earlier for a symmetric dichotomic process, $\nu_1=\nu_2=\nu$ at a Kubo number when $\sigma_\lambda^2/\nu^2\ll 1$ (see [42,43]). However, our estimations show that the expression (41) holds not only at $\sigma_\lambda^2/\nu^2\ll 1$ but also at $\sigma_\lambda^2/(\nu^2+\omega_0^2)\ll 1$ when $\sigma_\lambda^2\nu^2\ll\omega_0^4$. This allows us to draw the important conclusion. Even though the stochastic field initiates a damping process, it only leads to an equipartition of level population, i.e., $N_1(\infty)=N_2(\infty)=1/2$. And this equipartition does not depend on the energy difference E_1-E_2.

IV. SIMULTANEOUS ACTION OF THE STOCHASTIC FIELD AND THE THERMAL BATH

In this section we will investigate the influence of a stochastic field on relaxation processes initiated by the coupling

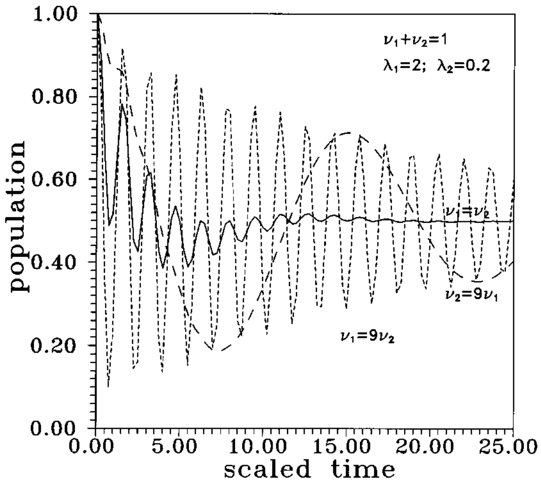

FIG. 1. Dependence of the level population $N_1(t)$ on time t (in arbitrary units) in the case of a degenerated TLS for the different jump frequencies ν_1 and ν_2. The jump amplitudes λ_1 and λ_2, and the autocorrelation time of the fluctuations $\tau=2/(\nu_1+\nu_2)$ are fixed.

to a TB. To specify the coupling to the TB we choose an expression known from the spin-boson model [10]. Hence, the system-TB interaction (5) will be fixed by the operator $\hat{F}_{nn'}$ of generalized forces according to

$$\hat{F}_{nn'}=\hat{F}_n\delta_{nn'},\quad \hat{F}_1=-\hat{F}_2\equiv\hat{F}=\hbar\sum_l \kappa_l(b_l^+ + b_l). \tag{42}$$

Here, κ_l serves as the coupling constant to the lth bath mode. Noting Eqs. (4), (5), (20), and (21) it becomes obvious that all elements of the relaxation matrix $\Gamma(t,t')$ can be expressed by the single correlation function

$$K(\tau)=K^*(-\tau)=\langle\Delta\hat{F}\Delta\hat{F}^{\tau}\rangle_B$$
$$=\sum_l \kappa_l^2[n(\omega_l)e^{i\omega_l\tau}+(1+n(\omega_l))e^{-i\omega_l\tau}], \tag{43}$$

where

$$n(\omega_l)=[\exp(\hbar\omega_l/k_BT)-1]^{-1} \tag{44}$$

denotes the Bose distribution function. For the sake of convenience we rewrite the correlation function (43) as

$$K(\tau)=\frac{1}{2\pi}\int_0^\infty[n(\omega)e^{i\omega\tau}+(1+n(\omega))e^{-i\omega\tau}]J(\omega)d\omega, \tag{45}$$

where $J(\omega)$ is the spectral strength of the TB [10,34,38],

$$J(\omega)=2\pi\sum_l \kappa_l^2\delta(\omega-\omega_l),\quad (\omega\geqslant 0). \tag{46}$$

The frequency dependence can be specified in relating this quantity to different models of an environment (see, e.g., the examples in [34,38,44]).

All types of further approximations strongly depend on the relation between the various parameters following from the dynamic model, the stochastic field, and the coupling to the TB. As in the foregoing section we consider the case of the degenerated and strongly nondegenerated TLS. In addition, we restrict ourselves to the weak-coupling limit with respect to the TB, i.e., $\kappa_l^2\ll\lambda_j^2$. The case of a strong coupling to the TB was already considered in [32].

A. The case of the degenerated TLS

Since $\omega_0=0$, the coherent part of the transfer in the TLS is determined by the quantities $\Delta_j=2\lambda_j$. The condition $\kappa_l^2\ll\Delta_j^2$ of a weak coupling to the TB coincides with the condition necessary to apply the Born approximation. To be more concrete we further specify the correlation function (43) to the case of a fast decay. (Model estimations of the spectral strength (46) result in decay times in the ps region [38].) In accordance with the results of Sec. II B non–Markovian effects are not essential in Eqs. (14) and (18) if the condition $\tau_r^{-1}\sim\kappa_l^2\tau_d\ll\tau_d^{-1}\approx\tau_b^{-1}$ is valid. Below we put $(\kappa_l\tau_b)^2\ll 1$, and, hence, one can apply the Markov approximation for the time scale of the order of τ_r. If $\tau_b^{-1}\gg\lambda_j$ the condition $(\kappa_l\tau_b)^2\ll 1$ replaces the inequality $\kappa_l^2\ll\lambda_j^2$ which holds in the case of the Born approximation. Besides, the inequality $(\kappa_l\tau_b)^2\ll 1$ allows us to extend the upper limit to ∞ in Eqs. (14) and (18). This supposition is in line with the discussion given in Sec. II B.

A further problem is related to the noise averaging of Eq. (14). It is well known that the decoupling $\overline{\Gamma(t)\rho(t)}=\overline{\Gamma(t)}\,\overline{\rho(t)}$ is correct at small Kubo numbers, i.e., at $\lambda_j\nu_j^{-1}\ll 1$. However, it is possible to show the following important property. If in the absence of any system-TB interaction, relaxation does not occur despite the presence of the stochastic field, the decoupling is valid at any relation between λ_j and ν_j. We take notice of this property in solving the equations for the level populations in the basis of the delocalized states $|+\rangle$ and $|-\rangle$. From Eqs. (20), (21), (42), and (43) we may derive that Eq. (14) splits off into two sets of equations. The first set determines the level populations $\rho_{++}(t),\rho_{--}(t)=1-\rho_{++}(t)$, whereas the second one is valid for the coherences $\rho_{+-}(t),\rho_{-+}(t)$. In the stochastic equation

$$\dot{\rho}_{++}(t)=-\Gamma_1(t)\rho_{++}(t)+\Gamma_2(t)\rho_{--}(t), \tag{47}$$

the relaxation parameters

$$\Gamma_1(t)=\frac{1}{\hbar^2}\int_0^\infty dt'[K^*(t-t')S_{+-;+-}(t,t')+K(t-t')S_{-+;-+}(t,t')], \tag{48}$$

$$\Gamma_2(t)=\frac{1}{\hbar^2}\int_0^\infty dt'[K^*(t-t')S_{-+;-+}(t,t')+K(t-t')S_{+-;+-}(t,t')]$$

are expressed by the elements of the stochastic dynamic matrix $S_0(t,t')$ [see Eq. (22)], and by the correlation function (43) of the TB. $\rho_{++}(t)$ is constant if the coupling to the TB has been neglected [see Eq. (37)]. The relaxation parameters $\Gamma_1(t)$ and $\Gamma_2(t)$ are retarded stochastic functionals of the intersite coupling $\lambda(t)$. Besides, they also incorporate the dissipative influence of the TB . Resulting from this, the relaxation constants define a rather complicated stochastic process with unknown properties. Nevertheless, one can conclude that the time scale of the stochastic evolution of $\Gamma_1(t)$ and $\Gamma_2(t)$ should correspond to the time scale ν^{-1}.

To obtain the noise averaged equation (48) the decoupling

$$\overline{\Gamma_j(t)\rho_{\mu\mu}(t)} \approx \overline{\Gamma_j}(t)\overline{\rho_{\mu\mu}}(t) \tag{49}$$

could be used. It works at small Kubo numbers of the induced stochastic process represented by $\Gamma_1(t)$ and $\Gamma_2(t)$. The Kubo number could be defined as $K_\Gamma = \Delta\Gamma/\nu$, where $\Delta\Gamma$ is the mean-square amplitude of the fluctuations of the relaxation parameters. Since $\Gamma_1(t),\ \Gamma_2(t) > 0$ at any time t, it is clear that $\Delta\Gamma$ cannot overcome τ_r^{-1}. Hence, we have $K_\Gamma \approx 1/\nu\tau_r \ll 1$, and the validity condition of the decoupling (49) corresponds to the fast fluctuations of $\lambda(t)$ on the time scale of the averaged relaxation process. Note, however, that the decoupling is valid at any relation between the frequencies ν_j and the amplitudes λ_j of the dichotomic field.

According to the averaging procedure given in Sec. III B we obtain $\overline{S_0}(t,t') = R(t-t')$ and, hence, we may write in Eq. (48) [in accordance with Eq. (34)] $\overline{S}_{+-;+-}(t,t') = M(t-t')$, and $\overline{S}_{-+;-+}(t,t') = M^*(t-t')$. Since the noise averaged kernels in Eqs. (48) depend on the time difference $t-t'$, the averaged quantities $k_j \equiv \overline{\Gamma_j}(t)$ do not depend on time t. As a result, the stochastic equation (47) is reduced to the averaged rate equation

$$\dot{N}_+(t) = -(k_1+k_2)N_+(t) + k_2, \tag{50}$$

with the noise averaged rate constants

$$k_1 = \int_0^\infty d\omega\, J(\omega)[I(\omega)(1+n(\omega)) + I(-\omega)n(\omega)], \tag{51}$$

$$k_2 = \int_0^\infty d\omega\, J(\omega)[I(\omega)n(\omega) + I(-\omega)(1+n(\omega))].$$

The spectral strength $J(\omega)$ is given by Eq. (46) and we had introduced

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\widetilde{M}(\omega),$$

$$\widetilde{M}(\omega) = \lim_{\eta\to+0}\int_0^\infty d\tau\, e^{-\eta\tau}e^{i\omega\tau}M(\tau). \tag{52}$$

A comparison between $\widetilde{M}(\omega)$ and the quantities (34) shows that $\widetilde{M}(\omega) = \widetilde{R}_{+-;+-}(-i\omega)$, and, hence, the stochastic characteristics are represented by the following structure of the spectral function $I(\omega)$ of the dichotomic process:

$$\begin{aligned} I(\omega) = {} & \frac{1}{\pi}\lim_{\eta\to+0}\frac{1}{\sqrt{r}}\Bigg\{\left(\frac{\nu_1+\nu_2}{2}+\eta\right) \\ & \times\left[\frac{(\omega-\Omega_-)\sin(\alpha/2)+(\gamma_-+\eta)\cos(\alpha/2)}{(\omega-\Omega_-)^2+(\gamma_-+\eta)^2} - \frac{(\omega-\Omega_+)\sin(\alpha/2)+(\gamma_++\eta)\cos(\alpha/2)}{(\omega-\Omega_+)^2+(\gamma_++\eta)^2}\right] \\ & + \left(\omega - 2\frac{\nu_1\lambda_1+\nu_2\lambda_2}{\nu_1+\nu_2}\right) \\ & \times\left[\frac{(\omega-\Omega_-)\cos(\alpha/2)-(\gamma_-+\eta)\sin(\alpha/2)}{(\omega-\Omega_-)^2+(\gamma_-+\eta)^2} - \frac{(\omega-\Omega_+)\cos(\alpha/2)-(\gamma_++\eta)\sin(\alpha/2)}{(\omega-\Omega_+)^2+(\gamma_++\eta)^2}\right]\Bigg\}. \end{aligned} \tag{53}$$

This expression is valid for $(\nu_1+\nu_2)^2 \geq 16(\lambda_1-\lambda_2)^2$. If $(\nu_1+\nu_2)^2 \leq 16(\lambda_1-\lambda_2)^2$ one has to replace α by $\pi-\alpha$. In Eq. (53) we may put $\eta = 0$ at arbitrary relations between parameters ν_j and λ_j, except the cases $\lambda_1 \approx \lambda_2$ and $\nu^2 \geq 4(\lambda_1-\lambda_2)^2$, when $\gamma_- \approx 0$.

The solution of Eq. (50) simply reads

$$N_\pm(t) = N_\pm(\infty) + [N_\pm(0) - N_\pm(\infty)]\exp[-(k_1+k_2)t], \tag{54}$$

with

$$N_+(\infty) = \frac{k_2}{k_1+k_2}, \quad N_-(\infty) = \frac{k_1}{k_1+k_2}. \tag{55}$$

The transition rate, $k = k_1+k_2$, as well as the equilibrium populations depend on the characteristic parameters of the stochastic field, ν_j and λ_j, [through the function $I(\omega)$] and on the coupling to the TB κ_l, [through the spectral strength $J(\omega)$]. If the stochastic alternation of the intersite coupling is reduced to the special case $\lambda_1 = \lambda_2 = \lambda$, the spectral function of the dichotomic process reduces to $I(\omega) = \delta(\omega - 2\lambda)$, and we have

$$k_1 = J(2\lambda)[1+n(2\lambda)], \quad k_2 = J(2\lambda)n(2\lambda). \tag{56}$$

This equation together with Eq. (44) demonstrate that the ratio $\xi(T) \equiv N_+(\infty)/N_-(\infty)$ between the equilibrium populations (55) reduces to the standard Boltzmann's factor

$$\xi(T) = k_2/k_1 = n(2\lambda)/[1+n(2\lambda)] = \exp(-2\hbar\lambda/k_BT). \tag{57}$$

Let us analyze the case where the intersite coupling obeys stochastic properties. We will do that for the special case of a symmetric dichotomic process. Putting in Eq. (53) $\nu_1 = \nu_2 = \nu$, at $\lambda_1 \neq \lambda_2$ we find two types of the spectral function,

$$I(\omega) = \frac{1}{\pi\sqrt{\nu^2 - 4(\lambda_1-\lambda_2)^2}} \times\left[\frac{\gamma_-(\nu-\gamma_-)}{(\omega-\Omega)^2+\gamma_-^2} - \frac{\gamma_+(\nu-\gamma_+)}{(\omega-\Omega)^2+\gamma_+^2}\right] \tag{58}$$

and

$$I(\omega)=\frac{\nu}{2\pi\sqrt{4(\lambda_1-\lambda_2)^2-\nu^2}}\left[\frac{\omega+\Omega-2\Omega_-}{(\omega-\Omega_-)^2+(\nu/2)^2}-\frac{\omega+\Omega-2\Omega_+}{(\omega-\Omega_+)^2+(\nu/2)^2}\right]. \tag{59}$$

Equation (58) is valid for $\nu^2\geqslant 4(\lambda_1-\lambda_2)^2$, whereas Eq. (59) is correct in the case $\nu^2\leqslant 4(\lambda_1-\lambda_2)^2$. In both equations we introduced the following shortenings:

$$\Omega=\lambda_1+\lambda_2,\quad \gamma_\pm=\tfrac{1}{2}(\nu\pm\sqrt{\nu^2-4(\lambda_1-\lambda_2)^2}),$$
$$\Omega_\pm=\Omega\pm\tfrac{1}{2}\sqrt{4(\lambda_1-\lambda_2)^2-\nu^2}. \tag{60}$$

At a high frequency of a dichotomic field, when $\nu^2\gg 4(\lambda_1-\lambda_2)^2$, expression (58) reduces to $I(\omega)=\delta(\omega-\Omega)$ and the intersite coupling is given as the sum $\lambda_1+\lambda_2$ of the possible amplitudes of the stochastic field. As a result, the transition rates are given by Eq. (56) with substitution of Ω by 2λ. In other words, the symmetric high-frequency dichotomic field does not break the equilibrium ratio between the forward and the backward transition rates initiated by a coupling to TB. This is not the case in the opposite limit of a low frequency of the dichotomic field, when $\nu^2\ll 4(\lambda_1-\lambda_2)^2$. Here the form (59) reduces to $I(\omega)=(1/2)[\delta(\omega-2\lambda_1)+\delta(\omega-2\lambda_2)]$, and the evolution process is achieved in two independent ways governed by the intersite coupling strengths λ_1 and λ_2 without any switching among them. It follows from Eq. (51) that in a low-frequency field the transition rates are

$$k_1=\frac{1}{2}\sum_{j=1,2}J(2\lambda_j)[1+n(2\lambda_j)],$$

$$k_2=\frac{1}{2}\sum_{j=1,2}J(2\lambda_j)n(2\lambda_j), \tag{61}$$

and, hence, the equilibrium ratio between both is only achieved in the case when one value of the spectral strength exceeds the other.

To obtain analytic results for the rate constants at an arbitrary stochastic field frequency ν, one needs to know the total frequency dependence of the spectral strength $J(\omega)$ based on a model of the TB. If, however, the coupling to the TB is large at a separate quantum mode of frequency $\omega_l=\Omega_0$, the spectral strength $J(\omega)$ may be reduced to $J(\omega)=2\pi\zeta^2\delta(\omega-\Omega_0)$, where ζ^2 is the square of the effective coupling at $\omega_l=\Omega_0$. A substitution of this form of $J(\omega)$ into Eqs. (51) results in the following rate expressions:

$$k_1=2\pi\zeta^2[(1+n(\Omega_0))I(\Omega_0)+n(\Omega_0)I(-\Omega_0)],$$
$$k_2=2\pi\zeta^2[n(\Omega_0)I(\Omega_0)+(1+n(\Omega_0))I(-\Omega_0)]. \tag{62}$$

The plots of the functions $I(\omega)$ and $I(-\omega)$, given in Fig.2, show that in a wide frequency region the function $I(\omega)$ considerably exceeds $I(-\omega)$. So, at a low temperature, when $n(\Omega_0)\ll 1$ and $n(\Omega_0)I(\Omega_0)\ll I(-\Omega_0)$, the ratio of the level populations is determined by the ratio of the spectral functions of the dichotomic process only, i.e., by

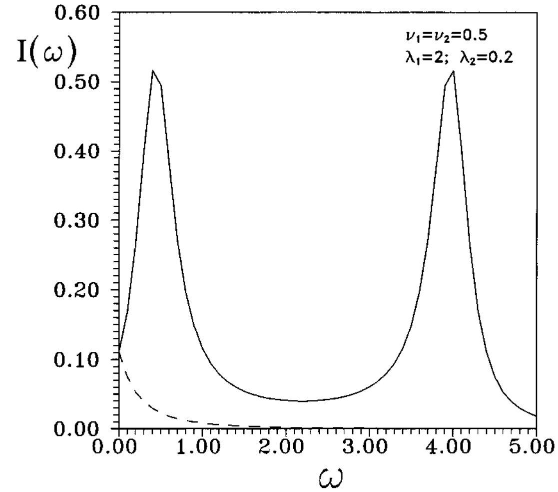

FIG. 2. Dependence of the spectral function $I(\omega)$ (solid line) and $I(-\omega)$ (dashed line), Eq. (59), on the frequency ω (in arbitrary units).

$$\xi(0)=\frac{I(-\Omega_0)}{I(\Omega_0)}=\frac{[(\Omega_0-\Omega)^2+\gamma_+^2][(\Omega_0-\Omega)^2+\gamma_-^2]}{[(\Omega_0+\Omega)^2+\gamma_+^2][(\Omega_0+\Omega)^2+\gamma_-^2]}, \tag{63}$$

at $\nu^2\geqslant(\lambda_1-\lambda_2)^2$, and by

$$\xi(0)=\frac{I(-\Omega_0)}{I(\Omega_0)}=\frac{[(\Omega_0-\Omega_-)^2+(\nu/2)^2][(\Omega_0-\Omega_+)^2+(\nu/2)^2]}{[(\Omega_0+\Omega_-)^2+(\nu/2)^2][(\Omega_0+\Omega_+)^2+(\nu/2)^2]} \tag{64}$$

at $\nu^2<4(\lambda_1-\lambda_2)^2$. Both expressions, (93) and (94), have their minimum at $\Omega=\Omega_0$ or $\Omega_\pm=\Omega_0$, and increase up to 1 when $\Omega\gg\Omega_0$ or $\Omega_\pm\gg\Omega_0$, respectively.

Such a behavior may allow us to propose a specific mechanism for a control of the transitions between extended states. This control can be achieved by varying the frequencies Ω and $\Omega_\pm$ through the amplitudes λ_1 and λ_2 of the dichotomous field. Additionally, in the frequency region $\nu^2<4(\lambda_1-\lambda_2)^2$ the control of the ratio k_2/k_1 can be realized by a variation of the frequency ν. Actually, let $\nu^2\ll 4(\lambda_1-\lambda_2)^2$, then $\Omega_+\approx 2\lambda_1$, $\Omega_-\approx 2\lambda_2$, and for $\Omega_+\approx\Omega_0$, or $\Omega_-\approx\Omega_0$, we have

$$\xi(T)=\frac{k_2}{k_1}\approx\frac{n(\Omega_0)+\xi(0)}{1+n(\Omega_0)}, \tag{65}$$

with $\xi(0)\ll 1$. In particular, when $n(\Omega_0)\gg\xi(0)$, the ratio (65) is transformed to the Boltzmann factor $k_2/k_1=\exp(-\hbar\Omega_0/k_BT)$. If one suddenly increases the amplitudes λ_j so that $\Omega_\pm\gg\Omega_0$ but $\nu^2<4(\lambda_1-\lambda_2)^2$ or $\nu^2\geqslant 4(\lambda_1-\lambda_2)^2$, the factors $\xi(0)$ and $\xi(T)$ are comparable to 1, and the forward and backward transition rates equal one

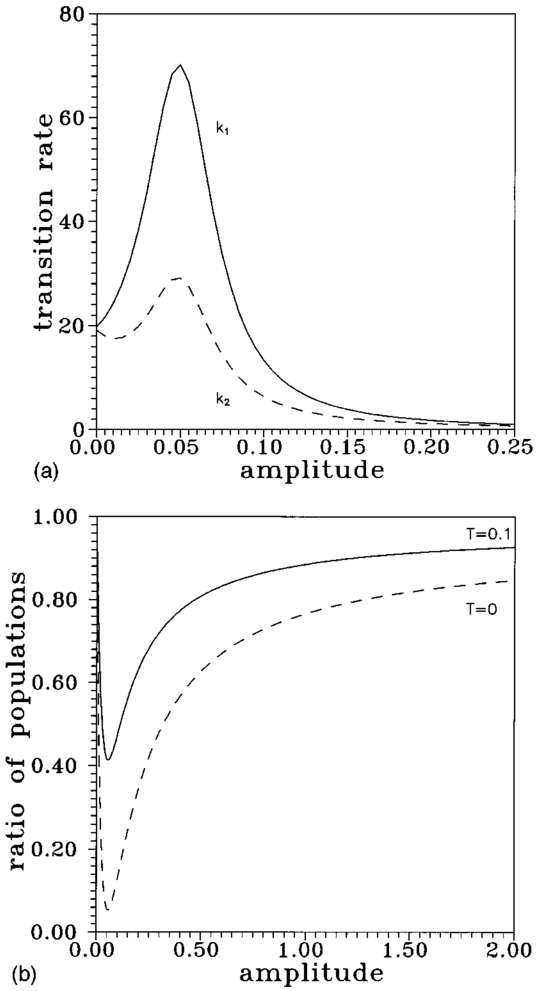

FIG. 3. (a) Dependence of the transition rates k_1 (solid line) and k_2 (dashed line), and (b) dependence of the ratio $\xi(T)$ Eq. (65), of the steady-state populations of the *eigenstates* on the amplitude of fluctuations λ_2 in the case of a degenerated TLS ($\lambda_1=3$, $\Omega_0=0.1$, and $\nu_1=\nu_2=0.1$). In (b), the solid line corresponds to the temperature $T=0.1$, and the dashed line corresponds to $T=0$. All quantities are given in arbitrary units.

another, i.e., $k_2/k_1=1$. Typical examples of the stochastic field influence on the forward and backward transition rates are shown in Fig. 3.

The above given analysis of the level-population evolution was formulated in the basis of the extended states $|+\rangle,|-\rangle$. However, in the degenerated case the localized and extended states fulfill the following relations:

$$|+\rangle\langle+|-|-\rangle\langle-|=|1\rangle\langle 2|+|2\rangle\langle 1|\equiv\hat{\sigma}_x,$$
$$|+\rangle\langle-|+|-\rangle\langle+|=-(|1\rangle\langle 1|-|2\rangle\langle 2|)\equiv-\hat{\sigma}_z, \quad (66)$$
$$|+\rangle\langle-|-|-\rangle\langle+|=-(|1\rangle\langle 2|-|2\rangle\langle 1|)\equiv-i\hat{\sigma}_y,$$

where $\hat{\sigma}_j$ are the Pauli matrices. Therefore, the rates k_1,k_2 and other related expressions simultaneously describe the evolution of the quantity $\overline{\rho_x(t)}\equiv\sigma_x(t)=\sigma_{12}(t)+\sigma_{21}(t)=N_+(t)-N_-(t)$. But to obtain the evolution of the averaged coherency $\overline{\rho_y(t)}\equiv\sigma_y(t)=i[\sigma_{12}(t)-\sigma_{21}(t)]=i[\sigma_{+-}(t)-\sigma_{-+}(t)]$ as well as the population difference $\overline{\rho_z(t)}\equiv\sigma_z(t)=\sigma_{11}(t)-\sigma_{22}(t)=-[\sigma_{+-}(t)+\sigma_{-+}(t)]$ it is necessary to average the set of stochastic equations

$$\begin{pmatrix}\dot{\rho}_{+-}(t)\\ \dot{\rho}_{-+}(t)\end{pmatrix}=-\left[i2\lambda(t)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}+\Gamma_\perp\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}\right]\times\begin{pmatrix}\rho_{+-}(t)\\ \rho_{-+}(t)\end{pmatrix} \quad (67)$$

with respect to realizations of $\lambda(t)=\lambda_1,\lambda_2$. Since the relaxation rate

$$\Gamma_\perp=\lim_{\omega\to 0}J(\omega)\coth(\hbar\omega/2k_BT) \quad (68)$$

is only expressed through the strength (46) and, hence, is not a stochastic quantity, the set (67) is similar to the equations for $\rho_z(t)$ and $\rho_y(t)$ derived and solved earlier in Ref. [30]. [To take advantage of the corresponding results one has to identify $2\lambda(t)\equiv L_0+\alpha(t)$, $2\Gamma_\perp=\xi$ in Eqs. (67).] For this reason we do not present the solutions of Eq. (67), but comment on the main physical results. First of all, we refer to the fact that the definite form of the relaxation term in Eq. (67) follows from the application of the Born and the Markov approximation. Necessary conditions for these approximations have been discussed at the end of Sec. II B and at the beginning of Sec. IV A. We add only that there is no need in carrying out a decoupling procedure that of Eq. (44) since $\Gamma_\perp$ is a nonstochastic quantity. Besides, the Born approximation is always valid if $\Gamma_\perp\ll\lambda_j$ at any relations between λ_j and ν. The Markov approximation is not only correct for the general relation $\tau_d\ll\tau_r\sim\Gamma_\perp^{-1}$, but also for the more specific condition $\tau_d\ll\nu^{-1},\lambda_j^{-1}$. The last one follows from the fact that after carrying out the average procedure the characteristic time scale of $\overline{\rho_{+-}(t)}$ is determined either by $\gamma_\pm^{-1}$ or $\Omega_\pm^{-1}$.

Our second comment is related to the asymptotic behavior of the level populations in the degenerated TLS. The stationary populations $N_1(\infty)\equiv\sigma_{11}(\infty)$ and $N_2(\infty)\equiv\sigma_{22}(\infty)$ are equal to one another, and the forward and backward transition rates (here, the transfer rates) coincide. Moreover, because the stochastic field influences the forward and backward transfer rates in the same manner, one can only control the total transfer process. Finally, by virtue of the Born approximation the general solution of Eq. (67) can easily be obtained from Eq. (38) since Eq. (38) is in fact the solution of Eq. (67) with $\Gamma_\perp=0$. If $\Gamma_\perp\neq 0$ but $\Gamma_\perp\ll\lambda_j$, the solution of Eq. (67) coincides with that of Eq. (38) where the substitution of $\tilde{\gamma}_\pm=\gamma_\pm+\Gamma_\perp$ for $\gamma_\pm$ must be performed. Thus the minor role of the coupling to the TB in the degenerated TLS and in the framework of the Born approximation is clearly seen. Only in the special case of a high-frequency stochastic field, i.e., at $\nu^2\gg 4(\lambda_1-\lambda_2)^2$, when $\gamma_+\approx\nu$, $\gamma_-\approx 0$, $\tilde{\gamma}_-=\Gamma_\perp$, the damping process, accompanying the transfer, depends on $\Gamma_\perp$ [see Eq. (38) at $\alpha\approx 0$, when $\Omega_+\approx\Omega_-=\Omega,\gamma_-\to\tilde{\gamma}_-\approx\Gamma_\perp,\gamma_+\to\tilde{\gamma}_+\approx\nu$]. However, the role of the coupling to the TB in the presence of a stochastic field is different for the transition processes between extended states of the TLS and for the transfer with strong coupling to the TB [31].

B. The case of the strongly nondegenerated TLS

Providing the inequality $\omega_0 \gg \lambda_j$ one can use the averaged GKE (12): In such a manner, the rather difficult procedure to average the GKE (14) can be circumvented. To obtain a detailed picture of the transfer process we carry out calculations at an arbitrary relation between ω_0 and ν_j. For this reason we cannot restrict ourselves to the Markov approximation. But, we apply the Born approximation with respect to the system-TB interaction, i.e., we put $(\kappa_l \tau_0)^2 \ll 1$ where $\tau_0^{-1} \sim \omega_0$.

To find the kernel (13) one should take into account that the dynamic matrix (9) is not a stochastic operator. According to Eqs. (4), (7), and (42) the quantity $\langle V \rangle_B$ vanishes and the averaged interstate coupling strength,

$$\overline{\lambda(t)} \equiv \overline{\lambda} = (\lambda_1 \nu_2 + \lambda_2 \nu_1)/(\nu_1 + \nu_2), \tag{69}$$

is independent of time, also the Hamiltonian H_D does not depend on time. As a result, the matrix (9) has a diagonal form

$$[S_D(t,t')]_{++;++} = [S_D(t,t')]_{--;--} = 1, \tag{70}$$

$$[S_D(t,t')]_{+-;+-} = [S_D(t,t')]^*_{-+;-+} = \exp[-i(\varepsilon_+ - \varepsilon_-)(t-t')/\hbar].$$

The *eigenvalues* ε_μ of the Hamiltonian $H_D = \Sigma_\mu \varepsilon_\mu |\mu\rangle\langle\mu|$ are given in Eq. (28) where the quantities $\alpha = 1,2$, $\varepsilon^{(j)}_{\alpha=1,2}$, Δ_j are substituted by $\mu = \pm$, $\varepsilon_{\mu=1.2}$, $\Delta = (\omega_0^2 + 4\overline{\lambda}^2)^{1/2}$, respectively. The *eigenstates* of H_D may be written as $|\mu\rangle = \Sigma_n u_{\mu n} |n\rangle$ where with accord to the inequality $\omega_0 \gg \lambda_j$ we have

$$u_{\mu 1} \approx \delta_{\mu +} + \delta_{\mu -} \sin\delta, \quad u_{\mu 2} \approx -\delta_{\mu +} \sin\delta + \delta_{\mu -}. \tag{71}$$

Here $\sin\delta \approx (\overline{\lambda}/\omega_0) \ll 1$. If we additionally take into consideration the inequality $(\kappa_l \tau_0)^2 \ll 1$, the mixture between the averaged level populations $\sigma_{++}(t)$ and $\sigma_{--}(t)$, and the averaged coherences $\sigma_{+-}(t)$ and $\sigma_{-+}(t)$ appears in higher approximations with respect to V only. In the framework of the Born approximation this mixing is omitted, and the GKE (12), determining the quantities $\sigma_z(t) = \sigma_{++}(t) - \sigma_{--}(t) \approx \sigma_{11}(t) - \sigma_{22}(t)$, reduces to the following master equation:

$$\dot{\sigma}_z(t) \approx -4\int_0^t dt' [4\sin^2\delta K_s(t-t') + Q(t-t')] \times \cos[\omega_0(t-t')]\sigma_z(t') - 16 i \sin^2\delta \int_0^t dt' K_a(t-t') \times \sin[\omega_0(t-t')]. \tag{72}$$

The correlation function (43) and the root-mean-square deviation σ_λ^2 from Eq. (41) are represented through the correlation functions

$$K_{s,a}(\tau) \equiv \tfrac{1}{2}[K(\tau) \pm K(-\tau)], \tag{73}$$

$$Q(\tau) = \overline{\lambda(\tau)\lambda(0)} - \overline{\lambda}^2 = \sigma_\lambda^2 \exp(-\nu\tau).$$

related to the TB and the stochastic field, respectively.

As a result of the Born approximation the solution of the non-Markovian master equation (72) coincides with the expression

$$\sigma_z(t) = -\frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2} + \left[\sigma_z(0) + \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}\right] \exp[-(\Gamma_1 + \Gamma_2)t] \tag{74}$$

which is true in the long-time limit. In Eq. (74) the forward (Γ_1) and backward (Γ_2) rates of the transfer are given by the expressions

$$\Gamma_1 = 8(\overline{\lambda}/\omega_0)^2 J(\omega_0)[1 + n(\omega_0)] + k_\parallel/2,$$

$$\Gamma_2 = 8(\overline{\lambda}/\omega_0)^2 J(\omega_0) n(\omega_0) + k_\parallel/2. \tag{75}$$

$k_\parallel$ denotes the longitudinal rate constant associated with a pure stochastic influence on the transfer [see Eqs. (39), (40)], and $J(\omega_0)$ is the spectral strength of the TB given by Eq. (46). Equations (74), (75) demonstrate that the steady populations $N_+(\infty) \approx N_1(\infty) = \Gamma_2/(\Gamma_1 + \Gamma_2)$ and $N_-(\infty) \approx N_2(\infty) = \Gamma_1/(\Gamma_1 + \Gamma_2)$, depend essentially on the relation between the two kinds of damping processes. This observation can be done despite the fact of the additive contribution of the transfer from two kinds of damping processes initiated by a coupling to the TB and an interaction with a stochastic field.

The ratio

$$\xi(T) \equiv \frac{N_1(\infty)}{N_2(\infty)} = \frac{\Gamma_2}{\Gamma_1} = \frac{n(\omega_0) + \beta}{1 + n(\omega_0) + \beta}, \tag{76}$$

$$\beta \equiv \frac{1}{4} \frac{\omega_0^2}{\omega_0^2 + \nu^2} \left(\frac{\sigma_\lambda}{\overline{\lambda}}\right)^2 \frac{\nu}{J(\omega_0)}$$

varies in a broad range. It starts at the Boltzmann factor $\exp(-\hbar\omega_0/k_B T)$, if the interaction with the TB largely exceeds the stochastic field influence, and ends up at 1, if the stochastic field influence dominates. For the spectral strength we may write $J(\omega_0) \approx \kappa_0^2 D(\omega_0)$, where κ_0 and $D(\omega_0)$ are, respectively, the main coupling to the TB and the density of the bath states near $\omega_l = \omega_0$. The boundaries of this region for ξ are given by the inequalities $\underline{\zeta^2} D(\omega_0) \gg (\nu/\omega_0^2)\sigma_\lambda^2$ and $(\nu/\omega_0^2)\sigma_\lambda^2 \gg \zeta^2 D(\omega_0)$, where $\zeta \equiv (\overline{\lambda}/\omega_0)\kappa_0$ is the effective coupling to the TB. Figure 4 displays the dependence of the ratio (76) on the parameters of the stochastic field.

V. CONCLUSIONS

The present paper has been devoted to clarifing the influence of two fundamentally different kinds of nuclear motions on quantum transitions. One type of nuclear motions is given by low-amplitude vibrations of the environment which are fast and which are assumed to be populated according to an equilibrium distribution. Following the standard treatment of such vibrational motion we attribute these vibrations to a thermal (heat) bath. Such an assumption cannot be used on the time scale of the transition process to characterize the high-amplitude twisting and flipping motions of large, separate molecular groups of the environment. The motion of each group exhibits a stochastic behavior and has been simu-

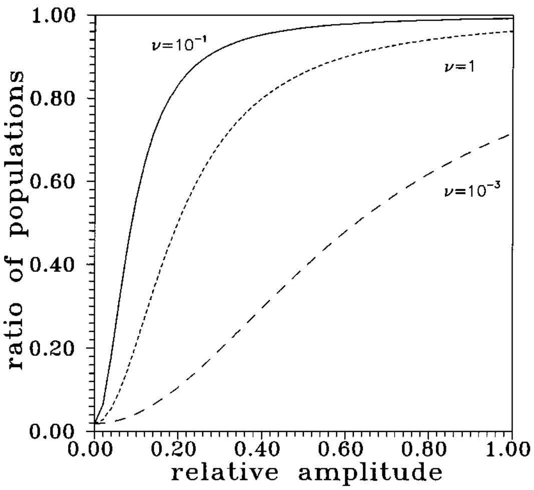

FIG. 4. Dependence of the ratio $\xi(T)$ Eq. (76), of the steady populations of the localized states on the relative amplitude of fluctuations, $\sigma_\lambda/\bar{\lambda}$ at the autocorrelation time $\tau=1/\nu$, in the case of a nondegenerated TLS [$\omega_0=0.1$, $J(\omega_0)=0.0001$, $\hbar\omega/k_BT=4$]. All quantities are given in arbitrary units.

lated by a stochastic field. Each kind of these two types of nuclear motion requires their own specific averaging procedure if one derives related GKE.

The averaging over the fast, low-amplitude nuclear vibrations is equivalent to the ensemble averaging over the TB states, and, hence, the ratio between any steady-state population of the energy levels in the considered system coincides with the Boltzmann factor $\exp(-\Delta\varepsilon/k_BT)$. The averaging with respect to the high-amplitude nuclear motions is reduced to the averaging with respect to the realizations of the stochastic parameters of the quantum system [in the considered case of the transfer to the intersite coupling strength $\lambda(t)$]. As a result, one can describe the influence of high-amplitude nuclear motions similar to external stochastic fields. I.e., one can include the specific stochastic properties of the environment directly into the Hamiltonian of a quantum system through corresponding parameters.

In contrast to the TB action, the stochastic field does not lead to the Boltzmann equilibrium ratio between steady-state populations but results in an equidistribution of occupation probability of the localized energy levels of a quantum system. This behavior appears despite the consideration of a nonzero energy difference between the quantum states [see Eq. (39)]. This distinction can be explained by the semiclassical nature of the high-amplitude nuclear motions. The transferring quantum particle (the quantum system in the general case) practically does not influence the high-amplitude nuclear motions and, thus, these motions are completely independent on the state of the quantum system. Since they have a stochastic character their action on the quantum particle can be understood as the action of an external stochastic field. On the time scale Δt of the transfer process the stochastic fields produced by the high-amplitude nuclear motions are nonequilibrium external fields. This is the reason for their description by means of a stochastic process instead of choosing a distribution function for their characterization.

In the case of the low-amplitude motions one observes an intensive energy exchange between the quantum system and this part of the environment. Owing to such an exchange and due to the fast relaxation within vibrational states, the TB supports the stationary Boltzmann ratio between corresponding populations and results in the irreversibility of the transfer. It is precisely the equilibrium energy exchange and the stochastic influence on a quantum particle that forms the specific ratio between the steady populations [see, for instance, Eqs. (65) and (76)].

The stochastic behavior of the environmental degrees of freedom can appear on the time scale of the transfer process if, e.g., macromolecular structures contain specific molecular groups controlling different transport pathways. As an example, we mention the flipping tyrosine ring embedded into an electron pathway [45], which statistically changes the donor-acceptor intersite coupling strength [46]. In numerous papers (see, for instance, Ref. [47]) the motion of such separated groups has been described in the framework of the stochastic theory. The description of high-amplitude nuclear motions in using discontinuous stochastic fields is the simplest way to take these motions into consideration. Such an approach does not desire the introduction of a specific Hamiltonian to include the above mentioned degrees of freedom. One must find only the physical model to determine the amplitudes and frequencies of the stochastic parameters for the desired quantum system rather than to solve the equations of motion for separated molecular groups of the environment. Such an approach was first proposed by Anderson [48] and Kubo [49].

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this work by the *Volkswagen–Stiftung* of the Federal Republic of Germany.

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