Dynamics of the dissipative two-level system driven by external telegraph noise

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The dissipative dynamics of a two-level system coupled to a thermal bath and driven by an external stochastic field is studied. Within an approach similar to the noninteracting-blip approximation, an integro-differential kinetic equation for the difference of the level populations averaged with respect to the bath is derived. An *exact* averaging of this kinetic equation is performed for the case of a dichotomous external force. The resulting equation is used to examine the long-range electron tunneling driven by external telegraph noise.

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I. INTRODUCTION

The two-level system (TLS) is of profound importance as the simplest fundamental model for the study of thermal relaxation and quantum tunneling phenomena in a number of physical and chemical systems [e.g., electron transfer reactions [1], proton tunneling [2,3], macroscopic quantum coherence in Josephson solid-state devices, superconducting quantum interference devices (SQUID's) [4,5], to mention a few]. To include the relaxation process (dissipation) one has to bring the TLS in contact with an environment. Usually the environment is modeled by a thermal bath of a large set of harmonic oscillators. The oscillators stay in equilibrium and are coupled linearly to the TLS. Using such a description of the environment, the dissipative TLS is mapped on the well-known spin-boson model [6]. This model has been extensively studied by many authors and in different aspects (see [6], and references therein).

However, there exist various systems where the description of the environment within a harmonic approximation is not quite correct. Such a situation arises, for example, in proteins, where the transfer of electrons between different sites may be influenced not only by (quasi) phonons but also by large-amplitude local excitations [7,8] (e.g., flipping of tyrosine rings or the rotation of surface residues [8]). These large-amplitude motions cannot be handled within the standard way of applying a harmonic approximation. Nevertheless, one can model such motions by means of a discrete stochastic process. Therefore one treats the stochastic process as an external stochastic field in the framework of time-dependent but harmonic theory. The dichotomous Markovian process (DMP, random telegraph signal) [9–11] is the simplest example of a relevant stochastic process. Using the DMP one can simulate, for example, the hopping of a relevant molecular group or ion between two equivalent positions. Besides, it may be treated as a truly external noise arising from an external dichotomous driving field. In contrast to the equilibrium noise produced by a harmonic (Gaussian) thermal bath, such a noise should be considered as a nonequilibrium one. The importance of the dichotomous model for the driving force is also connected with the possibility of its exact treatment. It is one of the motivations for our study.

In the following, we examine the effects of a dichotomous driving field on the dynamics of a dissipative two-level system. In Sec. II the general problem is formulated and we derive the kinetic equation in an approximation similar to the noninteracting-blip (NIB) approximation of the spin-boson model. The exact averaging of these equations over the dichotomous fluctuations of the energy bias is performed in Sec. III. Different extremes will be discussed and an exact expression for the average rate of incoherent relaxation will be presented. In Sec. IV we illustrate the elaborated theory in dealing with the dichotomically driven nonadiabatic electron transfer. Finally, the results are summarized in Sec. V and our conclusions are drawn.

II. MODEL AND THEORY

The model which we would like to investigate here is described by the Hamiltonian

$$H(t) = H_0(t) + H_{int} + H_T. \tag{1}$$

The first term,

$$H_0(t) = E_1(t)|1\rangle\langle 1| + E_2(t)|2\rangle\langle 2| + V(|1\rangle\langle 2| + |2\rangle\langle 1|), \tag{2}$$

describes the two states, $|1\rangle$ and $|2\rangle$, which are coupled by the intersite matrix element V. The time dependence of the state energies $E_1(t)$ and $E_2(t)$ in Eq. (2) results

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from time-dependent regular as well as stochastic external fields. The introduction of stochastic fields into the Hamiltonian of the dynamic system is well known from the Haken-Strobl-Reineker (HSR) model [12,13] which has been applied, e.g., to the excitation energy transfer in molecular systems [14,15]. In all these approaches the interaction with the thermal bath is described phenomenologically by a stochastic modulation of the site energies. Here, we include the system-bath interaction in a microscopic manner according to the second term in Eq. (1),

$$H_{int} = \frac{1}{2}\hat{F}(|1\rangle\langle 1| - |2\rangle\langle 2|)\ . \tag{3}$$

It introduces the fluctuations of the energy bias, $\varepsilon(t) = E_1(t) - E_2(t)$, caused by the thermal bath (TB). Here,

$$\hat{F} = \sum_\lambda \kappa_\lambda (b_\lambda^\dagger + b_\lambda) \tag{4}$$

is the bath-dependent operator of the generalized force which controls the energy bias fluctuations. κ_λ denotes the coupling constant, and b_λ, $b_\lambda^\dagger$ are the annihilation and creation operators of the λth state of the TB, respectively. The last term in Eq. (1) denotes the Hamiltonian of the TB formed by a set of independent harmonic oscillators with the (quasi) continuous spectrum $\{\omega_\lambda\}$,

$$H_T = \sum_\lambda \hbar\omega_\lambda (b_\lambda^\dagger b_\lambda + \tfrac{1}{2}). \tag{5}$$

It becomes simply obvious that Eqs. (1)–(5) are equivalent (despite an unimportant constant term) to the well-known spin-boson Hamiltonian [6] (generalized to the case of a time-dependent energy bias). To prove this statement, one has to replace the operators $|n\rangle\langle m|$ $(n, m = 1, 2)$ by quasispin 1/2 operators ($\hat{\sigma}_z = |1\rangle\langle 1| - |2\rangle\langle 2|$ and $\hat{\sigma}_x = |1\rangle\langle 2| + |2\rangle\langle 1|$) and the boson operators $b_\lambda, b_\lambda^\dagger$ by the momentum and position operators (p_λ and q_λ). However, the form (1)–(5) is more convenient for our goals, and hence it is utilized here. Using the well-known canonical displaced-oscillator transformation [16,17]

$$U = \exp[\tfrac{1}{2}\hat{R}(|\tilde{1}\rangle\langle\tilde{1}| - |\tilde{2}\rangle\langle\tilde{2}|)], \tag{6}$$

$$\hat{R} = \sum_\lambda \frac{\kappa_\lambda}{\hbar\omega_\lambda}(B_\lambda^\dagger - B_\lambda), \tag{7}$$

where, e.g., the new annihilation operator reads $B_\lambda = U^\dagger b_\lambda U$, one can represent the total Hamiltonian (1) in the basis of dressed states, $|\tilde{n}\rangle = U^\dagger |n\rangle$, as

$$\begin{aligned}\tilde{H}(t) &= U^\dagger H(t) U \\ &= E_1(t)|\tilde{1}\rangle\langle\tilde{1}| + E_2(t)|\tilde{2}\rangle\langle\tilde{2}| \\ &\quad + \sum_\lambda \hbar\omega_\lambda (B_\lambda^\dagger B_\lambda + \tfrac{1}{2}) + \hat{V}_{12}|\tilde{1}\rangle\langle\tilde{2}| + \hat{V}_{21}|\tilde{2}\rangle\langle\tilde{1}|.\end{aligned} \tag{8}$$

Here $\hat{V}_{12} = \hat{V}_{21}^\dagger = V\exp(\hat{R})$ is the operator of the dressed intersite coupling; the trivial constant energy term is omitted. In the transformed Hamiltonian (8), the sum of the first two terms can be considered as the Hamiltonian of the dressed TLS, $\tilde{H}_0(t)$, and the two last terms represent the coupling between the dressed TLS and the TB of the displaced oscillators [the third term in Eq. (8)]. Let us assume for simplicity that the dressed intersite coupling $\hat{V}_{12}$ becomes negligible after the averaging with respect to the TB,

$$\begin{aligned}\langle\hat{V}_{12}\rangle_T &= V\exp\left(-\frac{1}{4\pi}\int_0^\infty \frac{J(\omega)\coth(\hbar\omega/2k_BT)}{\omega^2}d\omega\right) \\ &\to 0.\end{aligned} \tag{9}$$

Here, the bath spectral function $J(\omega) = 2\pi\hbar^{-2}\sum_\lambda \kappa_\lambda^2\delta(\omega - \omega_\lambda)$ has been introduced [6], and the brackets $\langle\ \rangle_T$ denote the average over the thermal bath done with the equilibrium bath density matrix. The condition (9) is fulfilled if the spectral function behaves in the low-frequency range as $J(\omega) \sim \omega^\beta$ with $\beta \leq 2$. For example, Eq. (9) is valid in the important case of the Ohmic TB with $\beta = 1$. Otherwise, the two last terms in Eq. (8), averaged over the TB, should be included in the Hamiltonian of the dressed TLS. Such an incorporation would complicate essentially the problem, and, for this reason, the case $\beta > 2$ is not considered here.

Now, our nearest goal is to obtain the kinetic equation for the bath averaged difference, $\sigma_z(t) = \gamma_{11}(t) - \gamma_{22}(t)$, of the state populations $\gamma_{nn}(t) = \mathrm{Sp}[\tilde{\rho}(t)\tilde{\gamma}_{nn}]$ $(n = 1, 2)$. Here $\tilde{\rho}(t)$ is the reduced density matrix of the dressed TLS and $\tilde{\gamma}_{nn} = |\tilde{n}\rangle\langle\tilde{n}|$ is the corresponding population operator [18]. With this goal in mind, we consider the case of a weak intersite coupling V. In this case, the two last terms in Eq. (8) can be treated as perturbation in the lowest Born approximation. Then, the relevant kinetic equation can be reduced directly from the general kinetic equations for the state populations and coherences of a dissipative quantum system in an external field [19,17,20] utilizing the nonequilibrium density-matrix method [21]. As an alternative, one can apply the master equation of Argyres and Kelley [22] obtained in the framework of the projection-operator technique. Proceeding in this latter way [23], we write down the master equation in the basis of the operators $\tilde{\gamma}_{nm} = |\tilde{n}\rangle\langle\tilde{m}|$:

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}(t) = -\frac{i}{\hbar}[\tilde{H}_0(t), \tilde{\rho}(t)] - \frac{1}{\hbar^2}\int_0^t dt' \sum_{kk',rr'} \{&\langle\hat{V}_{rr'}(t)\hat{V}_{kk'}(t')\rangle_T[\tilde{\gamma}_{rr'}, \mho(t,t')\tilde{\gamma}_{kk'}\tilde{\rho}(t')] \\ &-\langle\hat{V}_{kk'}(t')\hat{V}_{rr'}(t)\rangle_T[\tilde{\gamma}_{rr'}, \mho(t,t')\tilde{\rho}(t')\tilde{\gamma}_{kk'}]\}.\end{aligned} \tag{10}$$

In Eq. (10), the quantities $\hat{V}_{kk'}(t) = \exp(iH_T/\hbar)\hat{V}_{kk'}\exp(-iH_T/\hbar)$ are the Heisenberg operators, and

$$\mho(t,t')\cdots = \hat{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t} d\tau[\tilde{H}_0(\tau),\ldots]\right) \tag{11}$$

is the evolution superoperator of TLS. Here $\hat{T}$ denotes Dyson's chronological operator. Note that Eq. (10) was obtained under the assumption that the TLS and the TB are decoupled at $t = 0$. Because of assumption (9) the evaluation of the time-ordered exponent in Eq. (11) becomes a trivial task (the Hamiltonian of the dressed TLS is diagonal). After some algebra we get from Eqs. (8)–(11) the desired kinetic equation:

$$\dot{\sigma}_z(t) = -\int_0^t f(t,t')\sigma_z(t')dt' - \int_0^t g(t,t')dt', \tag{12}$$

where

$$f(t,t') = f_0(t-t')\cos\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right), \quad g(t,t') = g_0(t-t')\sin\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right),$$

$$f_0(t) = \frac{4V^2}{\hbar^2}\exp[-G_s(t)]\cos[G_a(t)], \quad g_0(t) = \frac{4V^2}{\hbar^2}\exp[-G_s(t)]\sin[G_a(t)],$$

$$G_s(t) = \frac{1}{2\pi}\int_0^\infty \frac{J(\omega)}{\omega^2}\coth\left(\frac{\hbar\omega}{2k_BT}\right)(1-\cos\omega t)d\omega, \quad G_a(t) = \frac{1}{2\pi}\int_0^\infty \frac{J(\omega)}{\omega^2}\sin\omega t d\omega. \tag{13}$$

The functions $G_s(t)$ and $G_a(t)$ in Eq. (13) were introduced by Leggett *et al.* [6]. One can combine $G_s(t)$ and $G_a(t)$ to the complex function $G(t) = G_s(t) + iG_a(t)$. Then, G can be transformed in the function

$$G(t) = \int_0^t dt_1\int_0^{t_1}\langle\hat{F}(t_2)\hat{F}(0)\rangle_T dt_2 + i\frac{E_r}{\hbar}t\,. \tag{14}$$

This expression contains the autocorrelation function of the generalized force (4)

$$\langle\hat{F}(t)\hat{F}(0)\rangle_T = \frac{1}{2\pi}\int_0^\infty J(\omega)\frac{\cosh(\hbar\omega/2k_BT - i\omega t)}{\sinh(\hbar\omega/2k_BT)}d\omega\,, \tag{15}$$

and the bath reorganization energy

$$E_r = \sum_\lambda \frac{\kappa_\lambda^2}{\hbar\omega_\lambda} = \frac{\hbar}{2\pi}\int_0^\infty \frac{J(\omega)}{\omega}d\omega\,. \tag{16}$$

It should be stressed here that Eq. (12) includes driving forces in a nonperturbative manner. A similar kinetic equation was obtained also in [24], but using a different method. Virtually, the same kinetic equation can be deduced also from the general kinetic equations obtained in [19,17,20]. The only variation from Eq. (12) is that the lower limit of the integrals in Eq. (12) is changed to $-\infty$. Such a replacement reflects the different choice of the initial decoupling condition between TLS and TB: the *asymptotic* decoupling at $t \to -\infty$ in [19,17,20] and the *initial* decoupling at $t = 0$ in [22]. Which of them is more appropriate depends on the concrete physical formulation of the problem considered.

If the bias does not depend on time (ε =const), it can be easily checked in using the Laplace-transform method that Eqs. (12) and (13) give for the Laplace transform of $\sigma_z(t)$ the same result that was obtained within the so-called "noninteracting-blip approximation" in the path-integral approach [6]. A similar fact was established by Dekker [25,3] in the case of zero-energy bias, $\varepsilon = 0$. Therefore the kinetic equations (12) and (13) can be thought of as a generalization of the noninteracting-blip approximation (NIBA) to the case of time-dependent energy bias [26]. It can be used in a number of applications, including both regular and stochastic driving.

III. AVERAGING OVER DICHOTOMOUS PROCESS

Let us consider the case of a dichotomous driving force. We can write $\varepsilon(t) = \hbar\omega_0 + \hbar\Delta\alpha(t)$, where $\hbar\omega_0$ is the mean energy bias and $\hbar\Delta$ denotes the amplitude of the fluctuations. According to the chosen dichotomous Markov process we have $\alpha(t) = \pm 1$ with zero mean, $\langle\alpha(t)\rangle = 0$, and with exponentially decaying autocorrelation function [9–11], $\langle\alpha(t)\alpha(t')\rangle = \exp[-\nu(t-t')]$. The autocorrelation time of DMP is $\tau_0 = 1/\nu$. In what follows one has to average Eq. (12) over the different realizations of $\varepsilon(t)$. Generally, this is a nontrivial problem; however, in the case of dichotomous fluctuations it can be solved *exactly.* With this goal in mind, we proceed as follows [27]. Let us rewrite the kernels $f(t,t')$ and $g(t,t')$ in Eq. (12) in the form

$$\begin{aligned} f(t,t') &= f_0(t-t')\mathrm{Re}[e^{-i\omega_0(t-t')}S(t,t')], \\ g(t,t') &= -g_0(t-t')\mathrm{Im}[e^{-i\omega_0(t-t')}S(t,t')], \end{aligned} \tag{17}$$

where $S(t,t')$ is the evolution operator $S(t,t') = \exp[-i\Delta\int_{t'}^{t}\alpha(\tau)d\tau]$ of the celebrated Kubo oscillator [11] used in the stochastic theory of optical line shapes [28]. It obeys the stochastic evolution equation

$$\frac{d}{dt}S(t,t') = -i\Delta\alpha(t)S(t,t'),\ \ S(t',t') = 1. \tag{18}$$

To average Eq. (12) one has to evaluate the correlator $\langle S(t,t')\sigma_z(t')\rangle$. Therefore let us consider the formal expression

$$\langle S(t,t'+\tau)\alpha(t'+\tau)\alpha(t')\sigma_z(t')\rangle \ \ (\tau > 0)\ . \tag{19}$$

In Eq. (19) the quantities $S(t,t'+\tau)$ and $\sigma_z(t')$ are both functionals of the DMP $\alpha(t)$ involving only times posterior to $t'+\tau$ and prior to t', respectively. Therefore this expression meets the conditions of the theorem of Bourret, Frisch, and Pouquet (theorem B in [9]). According to this theorem we get

$$\langle S(t,t'+\tau)\alpha(t'+\tau)\alpha(t')\sigma_z(t')\rangle = \langle S(t,t'+\tau)\rangle\langle\alpha(t'+\tau)\alpha(t')\rangle\langle\sigma_z(t')\rangle + \langle S(t,t'+\tau)\alpha(t'+\tau)\rangle\langle\alpha(t')\sigma_z(t')\rangle. \tag{20}$$

Using the remarkable property of the DMP, $\alpha^2(t) = 1$, and passing to the limit $\tau \to +0$, we get the following corollary of theorem (20):

$$\langle S(t,t')\sigma_z(t')\rangle = S_0(t-t')\langle\sigma_z(t')\rangle + S_1(t-t')\langle\alpha(t')\sigma_z(t')\rangle, \tag{21}$$

where $S_0(t-t') = \langle S(t,t')\rangle$, and $S_1(t-t') = \langle\alpha(t')S(t,t')\rangle$. In the same way we obtain

$$\langle\alpha(t)S(t,t')\sigma_z(t')\rangle = S_1(t-t')\langle\sigma_z(t')\rangle + S_2(t-t')\langle\alpha(t')\sigma_z(t')\rangle, \tag{22}$$

where $S_2(t-t') = \langle\alpha(t)\alpha(t')S(t,t')\rangle$. In Eq. (22) we use the relations

$$S_1(t-t') = \frac{i}{\Delta}\frac{d}{dt}S_0(t-t') = -\frac{i}{\Delta}\frac{d}{dt'}S_0(t-t')\ ,$$
$$S_2(t-t') = \frac{1}{\Delta^2}\frac{d^2}{dtdt'}S_0(t-t') = -\frac{1}{\Delta^2}\frac{d^2}{dt^2}S_0(t-t')\ . \tag{23}$$

In a next step we will evaluate the averaged evolution operator $S_0(\tau)$. Such an averaged quantity as well as the equation of motion for the correlator $\langle\alpha(t)\sigma_z(t)\rangle$, arising in Eqs. (20), (21), can be carried out due to the theorem of Shapiro and Loginov [29]. It states

$$\frac{d}{dt}\langle\alpha(t)\Phi(t)\rangle = -\nu\langle\alpha(t)\Phi(t)\rangle + \left\langle\alpha(t)\frac{d}{dt}\Phi(t)\right\rangle \tag{24}$$

for any retarded functional $\Phi(t)$ of the DMP $\alpha(t)$. Applying this theorem to the correlator $\langle\alpha(t)S(t-t')\rangle$ on the right side of Eq. (18), and taking into account that $\alpha^2(t) = 1$, we get from Eq. (18) a closed set of differential equations for $S_0(t-t')$ and $S_1(t-t')$. The solution of these equations yields

$$S_0(\tau) = \exp\left(-\frac{\nu}{2}\tau\right)\left[\cosh\left(\frac{1}{2}\sqrt{\nu^2-4\Delta^2}\tau\right) + \frac{\nu}{\sqrt{\nu^2-4\Delta^2}}\times\sinh\left(\frac{1}{2}\sqrt{\nu^2-4\Delta^2}\tau\right)\right]. \tag{25}$$

A similar expression was found earlier in Refs. [11,28]. From Eq. (25) along with Eq. (23) we obtain the following expressions for the two remaining correlators:

$$S_1(\tau) = -\frac{2i\Delta}{\sqrt{\nu^2-4\Delta^2}}\exp\left(-\frac{\nu}{2}\tau\right)\times\sinh\left(\frac{1}{2}\sqrt{\nu^2-4\Delta^2}\tau\right),$$
$$S_2(\tau) = \exp\left(-\frac{\nu}{2}\tau\right)\left[\cosh\left(\frac{1}{2}\sqrt{\nu^2-4\Delta^2}\tau\right) - \frac{\nu}{\sqrt{\nu^2-4\Delta^2}}\sinh\left(\frac{1}{2}\sqrt{\nu^2-4\Delta^2}\tau\right)\right]. \tag{26}$$

Finally, applying the theorem (24) to the correlator $\langle\alpha(t)\sigma_z(t)\rangle$ and taking into account Eqs. (17), (21), (22), (25), and (26) one can get from Eq. (12) the exact closed set of integro-differential equations for the expectation value $\langle\sigma_z(t)\rangle$ and the correlator $\langle\alpha(t)\sigma_z(t)\rangle$:

$$\frac{d}{dt}\langle\sigma_z(t)\rangle = -\int_0^t\{S_0(t-t')f_0(t-t')\cos[\omega_0(t-t')]\langle\sigma_z(t')\rangle + iS_1(t-t')f_0(t-t')\sin[\omega_0(t-t')]\langle\alpha(t')\sigma_z(t')\rangle + S_0(t-t')g_0(t-t')\sin[\omega_0(t-t')]\}dt',$$
$$\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\nu\langle\alpha(t)\sigma_z(t)\rangle - \int_0^t\{S_2(t-t')f_0(t-t')\cos[\omega_0(t-t')]\langle\alpha(t')\sigma_z(t')\rangle + iS_1(t-t')f_0(t-t')\sin[\omega_0(t-t')]\langle\sigma_z(t')\rangle + iS_1(t-t')g_0(t-t')\cos[\omega_0(t-t')]\}dt', \tag{27}$$

with the initial conditions $\langle\sigma_z(0)\rangle = 1\,;\langle\alpha(0)\sigma_z(0)\rangle = 0$. Equation (27) along with Eqs. (25), (26) is the main result of our work. This result should be considered as a generalization of the NIBA to the case of dichotomically driven energy bias. It has the great advantage of accounting for the dichotomous driven force in an exact manner. Despite the rather complicated form, Eq. (27) can be useful in various applications. To show this, we restrict ourselves in the following to the case of zero mean energy bias, $\omega_0 = 0$. In this case, the set of equations (27) breaks down into two independent equations for the expectation $\langle\sigma_z(t)\rangle$ and the correlator $\langle\alpha(t)\sigma_z(t)\rangle$. As a result, we get

$$\frac{d}{dt}\langle\sigma_z(t)\rangle = -\int_0^t S_0(t-t')f_0(t-t')\langle\sigma_z(t')\rangle dt'. \tag{28}$$

Note that this rather nontrivial result appears as a consequence of the fact that the correlator $S_1(\tau)$ has no real part. It means that the factorization property, $\langle f(t,t')\sigma_z(t')\rangle = \langle f(t,t')\rangle\langle\sigma_z(t')\rangle$, holds, in the case considered, for an arbitrary autocorrelation time τ_0 of the DMP. A similar result, obtained after a separation of the equations of motion for $\langle\sigma_z(t)\rangle$ and $\langle\alpha(t)\sigma_z(t)\rangle$, within the spin-boson model extended by a dichotomically fluctuating intersite coupling [30], does not hold.

For the Laplace transform $\tilde{\sigma}_z(p) = \int_0^\infty \exp(-pt)\langle\sigma_z(t)\rangle dt$ we obtain from Eq. (28)

$$\tilde{\sigma}_z(p) = \left\{ p + \frac{1}{2}\left[\tilde{f}_0\left(p+\frac{\nu}{2}+\sqrt{\frac{\nu^2}{4}-\Delta^2}\right) + \tilde{f}_0\left(p+\frac{\nu}{2}-\sqrt{\frac{\nu^2}{4}-\Delta^2}\right)\right] - \frac{\nu}{2\sqrt{\nu^2-4\Delta^2}}\left[\tilde{f}_0\left(p+\frac{\nu}{2}+\sqrt{\frac{\nu^2}{4}-\Delta^2}\right) - \tilde{f}_0\left(p+\frac{\nu}{2}-\sqrt{\frac{\nu^2}{4}-\Delta^2}\right)\right]\right\}^{-1}, \tag{29}$$

where $\tilde{f}_0(p)$ is the Laplace transform of $f_0(t)$.

Consider now the different extremes of Eq. (29). In the absence of the external driving force ($\Delta = 0$) we have

$$\tilde{\sigma}_z(p) = \frac{1}{p+\tilde{f}_0(p)}. \tag{30}$$

Equation (30) is nothing else but the well-known result of the NIBA [6]. Another important example appears in the white-noise limit (see [9]), where $\nu,\ \Delta \to \infty$; $\eta = \Delta^2/\nu$ =const, where η is the white-noise intensity. In this case we get

$$\tilde{\sigma}_z(p) = \frac{1}{p+\tilde{f}_0(p+\eta)}. \tag{31}$$

The case $\Delta = \nu/2$ requires special treatment. By passing to the limit $\Delta \to \nu/2$ in Eq. (29), we obtain in this case

$$\tilde{\sigma}_z(p) = \frac{1}{p+\tilde{f}_0(p+\Delta)-\Delta\tilde{f}_0'(p+\Delta)} \quad [\tilde{f}_0'(p) = d\tilde{f}_0(p)/dp]\,. \tag{32}$$

Equations (29)–(32) provide the formal solution of the problem and describe generally multiexponential dynamics. The dynamics can be coherent or incoherent depending on the energetic structure of the TB, the strength of coupling between the TLS and the TB, the temperature, and the external field parameters. In the incoherent regime, it can be characterized by the effective relaxation rate $\Gamma = 1/\tau$, where

$$\tau = \int_0^\infty \langle\sigma_z(t)\rangle dt = \tilde{\sigma}_z(0) \tag{33}$$

is the mean first-passage time (the average relaxation time). Then, Eq. (29), along with Eq. (33), yields

$$\Gamma = \frac{1}{2}\left[\tilde{f}_0\left(\frac{\nu}{2}+\sqrt{\frac{\nu^2}{4}-\Delta^2}\right) + \tilde{f}_0\left(\frac{\nu}{2}-\sqrt{\frac{\nu^2}{4}-\Delta^2}\right)\right] - \frac{\nu}{2\sqrt{\nu^2-4\Delta^2}}\left[\tilde{f}_0\left(\frac{\nu}{2}+\sqrt{\frac{\nu^2}{4}-\Delta^2}\right) - \tilde{f}_0\left(\frac{\nu}{2}-\sqrt{\frac{\nu^2}{4}-\Delta^2}\right)\right]. \tag{34}$$

The influence of the external dichotomous driving force on the incoherent dynamics of a dissipative TLS can be traced from Eq. (34). To do this it requires a more detailed specification of the physical model for TLS.

IV. DICHOTOMOUSLY DRIVEN LONG-RANGE ELECTRON TRANSFER

Let us illustrate our theory in considering the bridge assisted long-range electron transfer (ET) driven by an external dichotomous field. In this case, the energy levels $E_1(t)$ and $E_2(t)$ may correspond to the states of a macromolecule well separated in space. The effective electronic coupling V between the two localized states results from the superexchange mechanism [31], and the relaxation rate Eq. (34) coincides with a transfer rate k_{tr}. Besides, the energy bias $\varepsilon(t)$ corresponds to the free-energy gap [1].

Consider for simplicity a situation where the mean value of the free-energy gap is zero, $\hbar\omega_0 = 0$, and assume that the ET is mediated by a single harmonic reaction coordinate coupled to an Ohmic thermal bath. In the case of the Ohmic thermal bath, this reaction coordinate is exposed to a frictional force linearly proportional to its velocity, and can be described by the effective spectral function [1,32,3,20]

$$J(\omega) = \frac{8\kappa_0^2}{\hbar^2} \frac{\gamma\Omega\omega}{(\Omega^2 - \omega^2)^2 + 4\gamma^2\omega^2} \tag{35}$$

in Eqs. (12), (13). Here Ω is the reaction coordinate frequency, κ_0 is the coupling constant between the transferred electron and the reaction coordinate, and γ is the broadening of the reaction coordinate levels due to the friction. In the strong coupling limit ($\kappa_0 \gg \hbar\Omega$) one can perform the short-time approximation for $G_{s(a)}(t)$ [1] or, which is the same, put $\langle \hat{F}(t)\hat{F}(0)\rangle_T \approx \langle \hat{F}^2(0)\rangle_T$ directly in Eq. (13). This procedure yields $G(t) \approx E_r k_B T_{eff} t^2/\hbar^2 + iE_r t/\hbar$, where $E_r = \kappa_0^2/\hbar\Omega$ is the reorganization energy of reaction coordinate and $T_{eff} = \hbar^2(4\pi k_B E_r)^{-1}\int_0^\infty \coth(\hbar\omega/2k_BT)J(\omega)d\omega$ is the effective temperature. The last one is a function of both the bath temperature and the friction [1]. At high temperatures we have $T_{eff} = T$. In the case of extremely weak friction ($\gamma \ll \omega_0$), one can use $k_BT_{eff} \approx \hbar\Omega/2\coth(\hbar\Omega/2k_BT)$ as a first order approximation. Other limiting cases for T_{eff} along with the detailed discussion can be found in [1]. Within the numerical calculations we shall restrict ourselves to the high-temperature limit. Under the above mentioned circumstances an approach similar to the noninteracting-blip approximation is appropriate. The ET takes place in the single-exponential, nonadiabatic regime [1], and we get for $\tilde{f}_0(p)$ the expression

$$\tilde{f}_0(p) = \frac{4\pi}{\hbar} \frac{V^2}{\sqrt{4\pi E_r k_B T_{eff}}} \mathrm{Re}[w(z)], \tag{36}$$

where $z = (E_r + i\hbar p)/2\sqrt{E_r k_B T_{eff}}$, $w(z) = \exp(-z^2)\mathrm{erfc}(-iz)$ is the error function of a complex variable, and $\mathrm{erfc}(z)$ is the complementary error function [33]. Equation (36) along with Eq. (34) provide the expression for the rate constant in the considered case. One can obtain a simple analytical expression of $k_{tr} = \Gamma$ for the following different extremes of the correlation time τ_0 and the amplitude $\hbar\Delta$ of energy gap fluctuations.

A. Weakly colored noise limit

Let us consider the case of weakly colored fluctuations when the Kubo number $K = \Delta\tau_0$ of the driving force is a small one, $K \ll 1$ [11]. With the assumption of fast fluctuations, and $\hbar\nu \gg (E_r k_B T_{eff})^{1/2}$, we get from Eqs. (34), (36)

$$k_{tr} = \frac{4\pi}{\hbar} \frac{V^2(1+K^2)}{\sqrt{4\pi E_r k_B T_{eff}}} \mathrm{Re}\left[w\left(\frac{E_r + i\hbar\eta}{2\sqrt{E_r k_B T_{eff}}}\right)\right]. \tag{37}$$

The white-noise limit is obtained from (37) by setting $K = 0$. Furthermore, if the noise intensity η is small, $\hbar\eta \ll E_r$, and the activation energy $E_a = E_r/4$ is not too large as compared to the k_BT_{eff}, the above equation reduces to the classical Marcus-Hopfield rate expression for the zero-energy gap case [34,35]. This rate expression contains the effective temperature T_{eff} instead of the bath temperature

$$k_{tr} \approx \frac{4\pi}{\hbar} \frac{V^2}{\sqrt{4\pi E_r k_B T_{eff}}} e^{-E_r/4k_BT_{eff}}. \tag{38}$$

We can conclude that the low-intensity noise does not influence the transfer rate in the case of small activation energy. Let us consider now the case where $(\hbar\eta)^2 + E_r^2 \gg 2E_r k_B T_{eff}$; then we have another extreme,

$$k_{tr} = \frac{4V^2}{\hbar^2} \frac{\eta}{\eta^2 + E_r^2/\hbar^2}. \tag{39}$$

The dependence (39) has a maximum at $\eta = E_r/\hbar$. The numerics show, however, that this maximum appears really only in the case of a large reorganization energy (Fig. 1). In the case of extremely intensive noise with $\hbar\eta \gg E_r$, $(E_r k_B T_{eff})^{1/2}$ we obtain

$$k_{tr} = \frac{4V^2}{\hbar^2}\frac{1}{\eta} \tag{40}$$

independently of the effective temperature and the reorganization energy (Fig. 1). The external noise controls the electron transfer in this limit completely.

Note that the results of this subsection are valid also for a weakly colored Gaussian Markovian noise with the same parameters τ_0 and Δ as the DMP.

B. Strongly colored noise limit

Consider now the case of a large Kubo number, $K \gg 1$. In this case we have

$$k_{tr} = \frac{2\pi}{\hbar} \frac{V^2}{\sqrt{4\pi E_r k_B T_{eff}}} \mathrm{Re}\left[w\left(\frac{\hbar\Delta + E_r + i\hbar\nu/2}{2\sqrt{E_r k_B T_{eff}}}\right) + w\left(\frac{\hbar\Delta - E_r + i\hbar\nu/2}{2\sqrt{E_r k_B T_{eff}}}\right)\right] \tag{41}$$

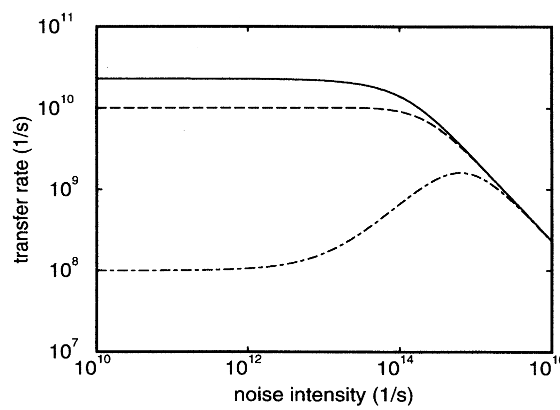

FIG. 1. Dependence of the transfer rates k_{tr} on the noise intensity η in the case of weakly colored noise, $K \ll 1$, at different reorganization energies. The set of parameters $T = 300$ K, $\hbar\omega_0 = 1 \times 10^{-2}$ eV, $V = 5 \times 10^{-4}$ eV, $E_r = 5 \times 10^{-2}$ eV (top curve), $E_r = 1 \times 10^{-1}$ eV (intermediate curve), and $E_r = 5 \times 10^{-1}$ eV (bottom curve) is used in the calculation.

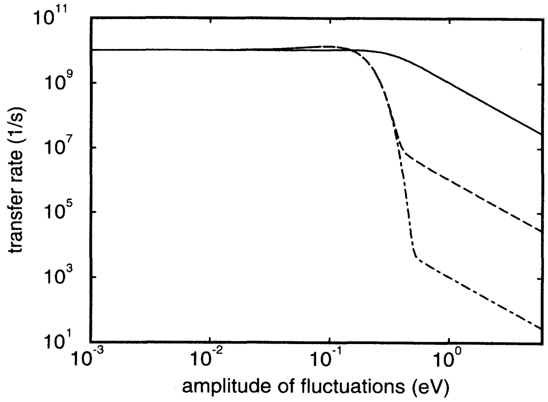

FIG. 2. Dependence of the transfer rates k_{tr} on the amplitude of fluctuations $\hbar\Delta$ at different autocorrelation time of fluctuations in the case of a small activation energy. The set of parameters $T = 300$ K, $\hbar\omega_0 = 1\times10^{-2}$ eV, $V = 5\times10^{-4}$ eV, $E_r = 1\times10^{-1}$ eV, $\tau = 10^{-3}$ ps (top curve), $\tau = 1$ ps (intermediate curve), and $\tau = 10^3$ ps (bottom curve) is used in the calculation.

as the first order approximation. For field-dependent activation energies $E_f(b) = (\hbar\Delta \mp E_r)^2/4E_r$ which are not too large in relation to $k_B T_{eff}$ we get from Eq. (41) the result of the quasistatic limit ($\tau_0 \to \infty$)

$$k_{tr} = \frac{2\pi}{\hbar}\frac{V^2}{\sqrt{4\pi E_r k_B T_{eff}}}[e^{-E_f/4k_BT_{eff}} + e^{-E_b/4k_BT_{eff}}]. \tag{42}$$

However, in the limit of a large amplitude, $\Delta \gg E_r$, the dependence of k_{tr} on the fluctuation field parameters is quite different (Figs. 2 and 3). In this case we obtain from Eq. (41)

$$k_{tr} \approx \frac{2V^2}{\hbar^2}\frac{\nu}{\Delta^2}. \tag{43}$$

Note that the dependence (43) is virtually the same as that of (40), however, the transfer rate in Eq. (43) is half of that in Eq. (40). The difference between the effects of the weakly colored noise (the top curve) and strongly colored noise (the bottom curves) on the transfer rate is clearly seen from Figs. 2 and 3. One can conclude that the strongly colored DMP is much more effective to control the transfer process than the weakly colored noise with the same amplitude. It can essentially suppress the dissipative tunneling.

C. The peculiar case, $\Delta = \nu/2$

In this case we get from Eqs. (32), (33), and (36) the rate expression

$$k_{tr} = \frac{4\pi}{\hbar}\frac{V^2}{\sqrt{4\pi E_r k_B T_{eff}}}\mathrm{Re}[w(z)] + \frac{2V^2\Delta}{E_r k_B T_{eff}}\{1 - \sqrt{\pi}\mathrm{Im}[zw(z)]\}, \tag{44}$$

where $z = (E_r + i\hbar\Delta)/2\sqrt{E_r k_B T_{eff}}$. Some numerics for this case are shown in Fig. 4. A comparison with Fig. 1 shows that, despite a principal distinction between the expression in Eq. (37) and Eq. (44), the behavior of the transfer rates with respect to the noise intensity Δ^2/ν (in the limit of weakly colored noise) or with respect to the amplitude of fluctuations Δ is similar. This fact reflects the similar nature of the influence of dichotomous noise on the kinetic processes at the Kubo number $K < 1$ (the peculiar case corresponds to $K = 1/2$).

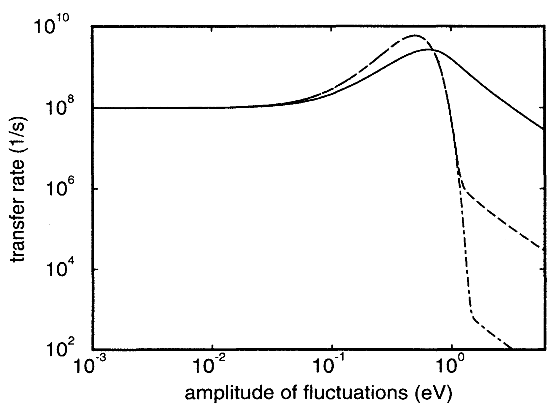

FIG. 3. Dependence of the transfer rates k_{tr} on the amplitude of fluctuations $\hbar\Delta$ at different autocorrelation time of fluctuations in the case of a large activation energy. The set of parameters $T = 300$ K, $\hbar\omega_0 = 1\times10^{-2}$ eV, $V = 5\times10^{-4}$ eV, $E_r = 5\times10^{-1}$ eV, $\tau = 10^{-3}$ ps (top curve), $\tau = 1$ ps (intermediate curve), and $\tau = 10^3$ ps (bottom curve) is used in the calculation.

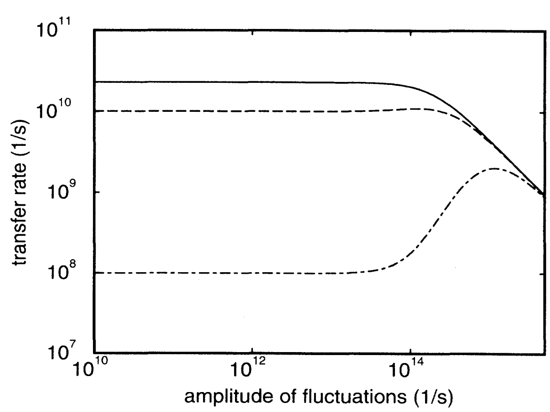

FIG. 4. Dependence of the transfer rates k_{tr} on the amplitude of fluctuations Δ in the peculiar case, $\Delta = \nu/2$, at different reorganization energies. The set of parameters $T = 300$ K, $\hbar\omega_0 = 1\times10^{-2}$ eV, $V = 5\times10^{-4}$ eV, $E_r = 5\times10^{-2}$ eV (top curve), $E_r = 1\times10^{-1}$ eV (intermediate curve), and $E_r = 5\times10^{-1}$ eV (bottom curve) is used in the calculation.

V. CONCLUSIONS

In conclusion, we outline briefly the main results of our study. Proceeding from the Argyres and Kelley master equation, we have obtained the integro-differential kinetic equation (12), (13) for the bath averaged difference of level populations of a time-dependent dissipative two-level system. The result was derived within an approach similar to the noninteracting-blip approximation with an exact inclusion of the external driving force. The equation obtained can be used in a large number of applications which include regular as well as stochastic driving forces. Furthermore, we arrived at an exact averaging of this kinetic equation in the case of the driving force modeled by the telegraph noise.

On the basis of stochastically averaged kinetic equation, we examined the effects of the fluctuating free-energy gap on the long-range electron transfer in a simple illustrative model. An analytical expression depending on the dichotomous fluctuation parameters was obtained for the transfer rate constant. It was shown that the external driving field can essentially modify the results of time-independent theory. Especially, it was manifested that the electron transfer rate can be either enhanced or reduced depending on the amplitude and the autocorrelation time of the dichotomous fluctuations, and on the bath reorganization energy. We found that the transfer rate is strongly dependent on the Kubo number K of the fluctuations. The different extremes of K are considered and corresponding simple analytical expressions for the transfer rate are obtained. It is deduced that dissipative tunneling can be drastically suppressed by the large-amplitude fluctuations in the limit of strongly colored noise.

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