Effective transfer rates for a dissipative two-level system driven by regular and stochastic fields

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The transfer processes in a two-level system coupled to a thermal bath and driven by strong regular and stochastic fields are studied. Starting with the master equation for a dissipative quantum system, the derivation of respective kinetic equations and effective transfer rates is demonstrated. For the low-temperature limit and the case of a large value of the reorganization energy of the environment it is shown that the action of a strong periodic field can invert the transfer process or block it completely. Applying an additional stochastic field, a weakening of this transfer blocking is obtained. [S1063-651X(96)50511-8]

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The dissipative two-level system (TLS) represents a basic model for the description of various transfer processes observed in crystals and molecular or biomolecular systems. Recently, considerable interest has been focused on the problem how to control transitions in the TLS by strong time-dependent fields. Using the dissipative TLS in the notation of the spin-boson problem and invoking the noninteracting blip approximation (NIBA) [1–8], it has been demonstrated that a fast oscillating field can change the transfer rates over orders of magnitude [4,9–11] and even can invert the transfer direction [10,11]. A similar control may also be initiated by stochastic fields as it could be shown in [7].

In the present paper the combined action of an external regular and stochastic field on the transfer process in a TLS will be studied. We start with the TLS Hamiltonian in the standard notation of the spin-boson system [1]

$$H(t)=\tfrac{1}{2}\,\varepsilon(t)\hat{\sigma}_z+V(t)\hat{\sigma}_x+\tfrac{1}{2}\,\hat{\sigma}_z\sum_{\lambda}\,\kappa_\lambda(b_\lambda^\dagger+b_\lambda)+\sum_{\lambda}\,\hbar\omega_\lambda(b_\lambda^\dagger b_\lambda+\tfrac{1}{2}), \tag{1}$$

where b_λ $(b_\lambda^\dagger)$ is the boson annihilation (creation) operator of the heat bath (HB) mode λ with frequency ω_λ, and $\hat{\sigma}_z=|1\rangle\langle 1|-|2\rangle\langle 2|$ and $\hat{\sigma}_x=|1\rangle\langle 2|+|2\rangle\langle 1|$ are the pseudospin operators defined by the TLS localized states $|1\rangle$ and $|2\rangle$. In Eq. (1), the time-independent quantity κ_λ is the coupling to the HB, whereas the energy bias $\varepsilon(t)=E_1(t)-E_2(t)$ and the tunneling coupling $V(t)$ depend on the driving field. To be more concrete we take

$$\varepsilon(t)=\varepsilon_0+\hbar A\cos\Omega t,$$

where ε_0 is the constant energy bias and A and Ω are the amplitude and the frequency of the bias oscillations, respectively. The stochastic field should influence the TLS via the tunneling coupling $V(t)$. We choose this quantity in such a manner that it randomly switches between two values V_1 and V_2 with escape frequencies ν_1 and ν_2, respectively [the dichotomous Markov process (DMP)].

To generalize the approach that is based on the NIBA and which yields a master equation for state population difference $\sigma_z(t)=\mathrm{tr}[\rho(t)\hat{\sigma}_z]$ [$\rho(t)$ is the reduced density matrix] we restrict ourself to the Born approximation with respect to the "dressed" internal coupling. Proceeding according to our former approaches [6,7,11], we obtain the stochastic master equation

$$\dot{\sigma}_z(t)=-\int_0^t V(t)V(t')f(t,t')\sigma_z(t')dt'-\int_0^t V(t)V(t')g(t,t')dt'. \tag{2}$$

The quantities

$$f(t,t')=\frac{4}{\hbar^2}\exp[-G_s(t-t')]\cos[G_a(t-t')]\times\cos\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right),$$

$$g(t,t')=\frac{4}{\hbar^2}\exp[-G_s(t-t')]\sin[G_a(t-t')]\times\sin\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right), \tag{3}$$

define the regular part of the integral kernels contained in the master equation. They include the contribution of the HB and the regular field. The function $G(t)=G_s(t)+iG_a(t)$ [1] accounts for the influence of the HB and can be represented as

$$G(t)=\int_0^t dt_1\int_0^{t_1}K(t_2)dt_2+i\frac{E_r}{\hbar}t, \tag{4}$$

where

$$K(t)=\frac{1}{2\pi}\int_0^\infty d\omega J(\omega)\,\frac{\cosh(\hbar\omega/2k_BT-i\omega t)}{\sinh(\hbar\omega/2k_BT)} \tag{5}$$

is the autocorrelation function of the energy bias fluctuations caused by the HB. This function, as well as the bath reorganization energy

$$E_r=\sum_\lambda \frac{\kappa_\lambda^2}{\hbar\omega_\lambda}=\frac{\hbar}{2\pi}\int_0^\infty \frac{J(\omega)}{\omega}d\omega, \qquad (6)$$

includes the spectral density of the bath

$$J(\omega)=\frac{2\pi}{\hbar^2}\sum_\lambda \kappa_\lambda^2\delta(\omega-\omega_\lambda). \qquad (7)$$

The main goal of the present study is to derive the master equation for the difference of the state populations $\langle\overline{\sigma_z(t)}\rangle$ averaged with respect to realizations of the random tunneling coupling $V(t)$ (which will be denoted by $\langle\,\rangle$) and averaged with respect to the oscillations of the periodic field (indicated by an overbar). Similar master equations were derived earlier either for the case of the periodic field [4,8–11] or for the case of the DMP [6,7]. The generalization to the combined action of both types of external fields depends essentially on the relation between the mean arithmetic escape frequency $\nu=(\nu_1+\nu_2)/2$ of the DMP, the frequency Ω of the periodic field, and the reverse relaxation time τ_r^{-1} stemming from the coupling to the HB. Here we restrict ourselves to the rather important frequency region $\Omega\gg\nu\gg\tau_r^{-1}$ only. In this case, the first step of the averaging procedure is related to the averaging with respect to the fast oscillations of the periodic field. In line with the treatment of [4,6–9,11] we obtain

$$\frac{d}{dt}\overline{\sigma_z}(t)=-\int_0^t V(t)V(t')\overline{f(t-t')}\,\overline{\sigma_z}(t')dt' - \int_0^t V(t)V(t')\overline{g(t-t')}dt'. \qquad (8)$$

The functions

$$\overline{f(t-t')}=\frac{4}{\hbar^2}\exp[-G_s(t-t')]\cos[G_a(t-t')] \times\sum_{n=-\infty}^{\infty} J_n^2\left(\frac{A}{\Omega}\right)\cos[(\Omega_0+n\Omega)(t-t')],$$

$$\overline{g(t-t')}=\frac{4}{\hbar^2}\exp[-G_s(t-t')]\sin[G_a(t-t')] \times\sum_{n=-\infty}^{\infty} J_n^2\left(\frac{A}{\Omega}\right)\sin[(\Omega_0+n\Omega)(t-t')] \qquad (9)$$

contain $\Omega_0\equiv\varepsilon_0/\hbar$ and the Bessel function $J_n(z)$ of the first kind, which describes the influence of multiphoton processes on the transfer reaction. Since $V(t)$ and $\overline{\sigma_z}(t)$ of Eq. (8) are random quantities, the noise averaging of Eq. (8) has to be carried out in the next step. (In the case of a symmetric DMP the noise averaging is possible in an exact manner [6,7,12,13].) Below we apply the standard decoupling

$$\langle V(t)V(t')\overline{\sigma_z}(t')\rangle=\langle V(t)V(t')\rangle\langle\overline{\sigma_z}(t')\rangle,$$

which is valid at small Kubo numbers $K_j\equiv V_j/\nu\hbar\ll 1$ [14,15]. Furthermore, we can use the exact relation $\langle V(t)V(t')\rangle=\sigma_V^2\exp(-\nu|t-t'|)+\langle V\rangle^2$, where

$$\sigma_V^2=\nu_1\nu_2(V_1-V_2)^2/4\nu^2$$

and

$$\langle V\rangle=(V_1\nu_2+V_2\nu_1)/2\nu$$

are the root-mean-square deviation and the noise-averaged internal coupling, respectively. Proceeding in such a way, we get from Eq. (8) the completely averaged master equation

$$\frac{d}{dt}\langle\overline{\sigma_z(t)}\rangle=-\int_0^t\{\langle V\rangle^2+\sigma_V^2\exp[-\nu(t-t')]\overline{f(t-t')}\} \times\langle\overline{\sigma_z}(t')\rangle dt' - \int_0^t\{\langle V\rangle^2+\sigma_V^2\exp[-\nu(t-t')])\} \times\overline{g(t-t')}dt'. \qquad (10)$$

This equation forms the desired basis for the study of averaged transfer processes in a TLS. The contained memory effects are of minor importance if the decay time τ_d of these functions is rather small compared to the relaxation time τ_r. Then, on the time scale $\Delta t\sim\tau_r\gg\tau_d$, the upper limit in the integrals of Eq. (10) can be replaced by ∞ and Eq. (10) reduces to the balance equations

$$\dot P_1(t)=-k_fP_1(t)+k_bP_2(t),$$

$$\dot P_2(t)=-k_bP_2(t)+k_fP_1(t)$$

for the averaged populations $P_1(t)=[1+\langle\overline{\sigma_z(t)}\rangle]/2$ and $P_2(t)=[1-\langle\overline{\sigma_z}(t)\rangle]/2$. The forward k_f and backward k_b effective transfer rates read

$$k_{f,b}=\sum_{n=-\infty}^{\infty}J_n^2\left(\frac{A}{\Omega}\right)[\langle V\rangle^2\tilde f_{n\pm}(0)+\sigma_V^2\tilde f_{n\pm}(\nu)], \qquad (11)$$

where

$$\tilde f_{n\pm}(\nu)=\frac{2}{\hbar^2}\mathrm{Re}\int_0^\infty dt\exp[-G(t)\pm i(\Omega_0+n\Omega)t-\nu t]. \qquad (12)$$

The expression (11) of the rate constants enables us to calculate the total effective transfer rate

$$k=k_f+k_b$$

as well as the steady-state populations

$$P_{1,2}^s=k_{b,f}/(k_f+k_b).$$

It is necessary to note that the ratio of the steady-state populations does not coincide with the conventional Boltzmann form $\exp[-(\varepsilon_0/k_BT)]$ of thermal equilibrium obtained at a small tunneling coupling. Both types of external fields drive the quantum system out of the thermal equilibrium. This effect can be characterized by means of the effective energy gap $\varepsilon_{\rm eff}$ introduced via the expression

$$P_1^s/P_2^s=\exp(-\varepsilon_{\rm eff}/k_BT),$$

which results in

$$\varepsilon_{\rm eff}=k_BT\ln(k_f/k_b).$$

For a further quantitative analysis of the transfer processes it is necessary to specify the function $G(t)$ defined in Eq. (4)

and, respectively, the spectral density $J(\omega)$ [2,16,17]. Here we restrict ourselves to the model where the TLS is coupled to a set of low-frequency modes and a single quantum mode of the environment. Thus we have

$$J(\omega)=J_{\rm LF}(\omega)+J_{\rm quant}(\omega).$$

The first contribution

$$J_{\rm LF}(\omega)=\frac{2\pi E_r}{\hbar\omega_D}\omega\Theta(\omega_D-\omega) \tag{13}$$

reflects the Ohmic form of the spectral density with an abrupt cutoff at the Debye cutoff frequency ω_D [2]. $\Theta(x)$ is the unit step function and E_r denotes the part of the reorganization energy (6), which corresponds to the low-frequency vibrations. The second contribution

$$J_{\rm quant}(\omega)=\frac{2\pi\kappa_0^2}{\hbar^2}\delta(\omega-\omega_0) \tag{14}$$

describes the strong coupling (with coupling strength κ_0) to the specific high-frequency quantum mode of the environment (or to an intramolecular reaction coordinate) with frequency ω_0.

The analytical evaluation of the low-frequency (LF) part of the spectral density (13) is possible in the short-time approximation when

$$K_{\rm LF}(t)\approx K_{\rm LF}(0)=\Delta^2=\int_0^\infty d\omega J_{\rm LF}(\omega)\coth(\hbar\omega/2k_BT)/2\pi. \tag{15}$$

Since the oscillatory decay of $K_{\rm LF}(t)$ is exclusively defined by the Debye cutoff frequency ω_D, the justification of Eq. (15) follows directly from the condition $\Delta\gg\omega_D$. The asymptotic relations $\Delta^2\approx 2E_rk_BT/\hbar^2$ and $\Delta^2\approx E_r\omega_D/2\hbar$, valid at high temperatures ($k_BT\gg\hbar\omega_D$) and low temperature ($k_BT\ll\hbar\omega_D$), respectively, show clearly that the inequality $\Delta\gg\omega_D$ is definitely fulfilled in the case of a high reorganization energy when $E_r\gg\hbar\omega_D$. Such an inequality is typical for molecular systems embedded in nonpolar media and we may stress that the short-time approximation (15) can be used at any temperature. To present an estimation we will take below $E_r=50\ \mathrm{cm}^{-1}$ and $\hbar\omega_D=5\ \mathrm{cm}^{-1}$ ($\omega_D^{-1}\sim 1$ ps) [18]. (In polar media E_r is much larger [19].) Using the analytic expressions (14) and (15) for the total spectral strength (13) it follows that

$$e^{-G(t)}=e^{-G_0}\sum_{p=-\infty}^{\infty}I_{|p|}(x)e^{-p\hbar\omega_0/2k_BT}e^{i(p\omega_0-E_r/\hbar)t}e^{-\Delta^2t^2/2}. \tag{16}$$

$G_0=S\coth(\hbar\omega_0/2k_BT)$ is the quantum part of the Debye-Waller factor, $S=\kappa_0^2/(\hbar\omega_0)^2$ denotes the dimensionless coupling strength between the TLS and the specific quantum mode, and $x=S\,\mathrm{csch}(\hbar\omega_0/2k_BT)$ is the argument of the modified Bessel function $I_p(x)$ of the pth order. Then, in accordance with Eqs. (12) and (16) we obtain

$$\tilde{f}_{n\pm}(\nu)=\frac{2\pi}{\hbar^2}e^{-G_0}\sum_{p=-\infty}^{\infty}I_{|p|}(x)e^{-p\hbar\omega_0/2k_BT}\times\Phi_\nu((-E_r\pm\varepsilon_0)/\hbar+p\omega_0+n\Omega), \tag{17}$$

where $\Phi_\nu(x)=\mathrm{Re}[w((x+i\nu)/\sqrt{2}\Delta)]/\sqrt{2\pi}\Delta$. Here $w(z)=\exp(-z^2)\mathrm{erfc}(-iz)$ denotes the error function of a complex variable and $\mathrm{erfc}(z)$ is the complementary error function. At $\nu=0$ and in the high-temperature limit $k_BT\gg\hbar\omega_D$, the line shape is Gaussian, i.e., $\Phi_0(x)=\exp[-(\hbar x)^2/4E_rk_BT]/\sqrt{4\pi E_rk_BT}$ and we obtain the result derived previously in [4,9–11]. The width of the line shape function is given by the low-frequency part of the HB spectral density and the stochastic fluctuations of the tunneling coupling. It is finite even at $T=0$, which reflects the quantum-mechanical nature of the HB. If $\nu\neq 0$, $\Phi_\nu(x)$ has Lorentzian wings at large x, and if $\nu\gg\Delta$, the Gaussian form is transformed into a Lorentzian form $\Phi_\nu(x)=\nu/\pi(\nu^2+x^2)$. Generally, we can state that stochastic fluctuations result in a broadening of the line-shape function.

Let us concentrate on the low-temperature limit to have a simple example for the alternation of transfer rates by external fields. Taking Eqs. (11) and (17) and carrying out the limit $T\to 0$, one obtains the transfer rates

$$k_{f,b}=\frac{\sqrt{2\pi}}{\hbar^2\Delta}e^{-S}\sum_{p=0}^{\infty}\frac{S^p}{p!}\sum_{n=-\infty}^{\infty}J_n^2\left(\frac{A}{\Omega}\right)[\langle V\rangle^2\Phi_0(E_r/\hbar\mp\Omega_0+p\omega_0+n\Omega)+\sigma_V^2\Phi_\nu(E_r/\hbar\mp\Omega_0+p\omega_0+n\Omega)], \tag{18}$$

which describe a pure tunneling process.

In a first step, let us consider the limit of low-frequency bias oscillations where $\Omega\ll\Delta$. In this case one can replace the summation with respect to the index n in Eq. (18) by an integration in considering n as a continuous number. If one further assumes that $J_n(A/\Omega)$ is a smooth function of n in the vicinity of the maximum of the line-shape function

$$n_\pm(p)\equiv[\pm\Omega_0-p\omega_0-E_r/\hbar]/\Omega,$$

one can factor out $J_{n_\pm(p)}(A/\Omega)$ from the integral. The remaining integral yields $1/\Omega$ *independently* on Δ and ν. As a result, we get

$$k_{f,b}\approx\frac{2\pi}{\hbar^2\Omega}\langle V^2\rangle e^{-S}\sum_{p=0}^{\infty}\frac{S^p}{p!}J^2_{n_\pm(p)}\left(\frac{A}{\Omega}\right), \tag{19}$$

where $\langle V^2\rangle=\langle V\rangle^2+\sigma_V^2$ is the mean-square value of the intersite coupling. Note that in the given approximation the stochastic fluctuations lead only to a renormalization of the tunneling coupling.

This approximation can be used to demonstrate the possible inversion and blocking of the transfer reaction that appears at nonzero energy bias $\varepsilon_0\neq 0$. To obtain analytic results we consider the form (19) at $S<1$. In this case the terms having a large p give only small contributions to the sum. If we assume $(A/\Omega)\gg|n_\pm(p)|$ for all important p, the asymptotic form of the Bessel function $J_n(x)$ can be used for the calculation. We obtain

$$k_{f,b}\approx\frac{4\langle V^2\rangle}{\hbar^2A}e^{-S}\sum_{p=0}^{\infty}\frac{S^p}{p!}\cos^2\left[\frac{A}{\Omega}-\frac{n_\pm(p)\pi}{2}-\frac{\pi}{4}\right]. \tag{20}$$

Let $\Omega=\omega_0/2m$, where m is a number large enough to ensure $\Omega\ll\Delta$. Then, after carrying out the summation we get a rather simple form for the effective rate constants

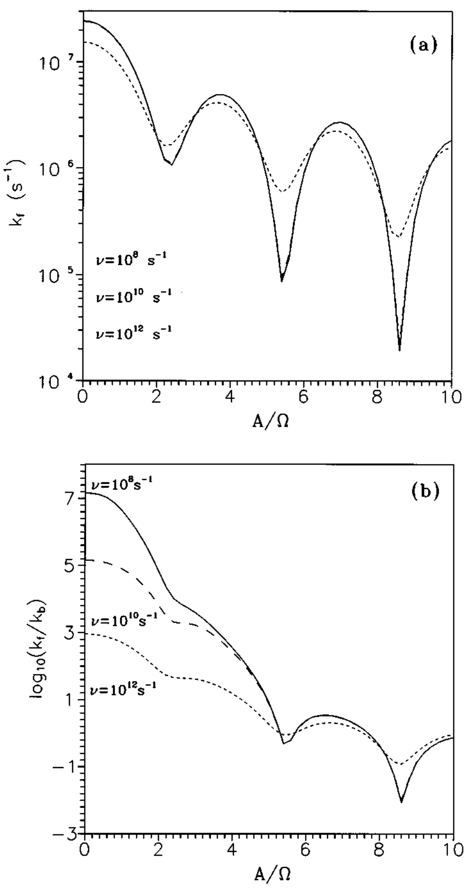

FIG. 1. (a) Dependence of k_f and (b) of k_f/k_b on A/Ω at three different values of ν. The low-temperature limit $k_BT \ll \hbar\omega_D, \hbar\omega_0$ has been considered in using the following set of parameters: $\varepsilon_0 = 0.1$ eV, $\hbar\omega_0 = 0.047$ eV, $E_r = 0.006$ eV≈ 50 cm^{-1}, $\hbar\omega_D = 5$ cm^{-1}, $\hbar\Omega = 0.025$ eV, $\langle V\rangle = 0.1$ cm^{-1}, $\sigma_V = 0.1$ cm^{-1}, and $S = 1$. (Note that the rates k_f at $\nu = 10^8$ s^{-1} and $\nu = 10^{10}$ s^{-1} practically coincide.)

$$k_{f,b} \approx \frac{4\langle V^2\rangle}{\hbar^2 A}\cos^2\left[\frac{A}{\Omega} - \frac{n_\pm(0)\pi}{2} - \frac{\pi}{4}\right]. \tag{21}$$

If $n_+(0) - n_-(0) = \Omega_0/\Omega \neq l$ $(l = 1,2,3, \ldots)$ the forward rate vanishes at field amplitudes

$$A \equiv A_r = \Omega\left[r\pi + \frac{n_+(0)\pi}{2} + \frac{3\pi}{4}\right], \tag{22}$$

whereas the backward rate remains finite (*the inversion effect*). If $\Omega_0/\Omega = l$, both rates coincide, which is similar to the case of the isoenergetic transfer ($\Omega_0 = 0$). Therefore, if the condition (22) is valid the transfer process in the TLS can be blocked completely.

Note, however, that the approximation (19) is indeed a rather crude one. In particular, it is questionable at $\Omega \sim \Delta$ and it is definitely invalid for $\Omega \gg \Delta$. Hence a numerical calculation is necessary. But before doing this some general conclusions can be drawn. In the present case of interest only contributions to the sum (18) with integer n and positive integer p are essential, which, roughly speaking, are the solutions of the inequality

$$|n\Omega + p\omega_0 + E_r/\hbar \mp \Omega_0| < \Delta.$$

Let us assume for a moment that $\Delta = 0$ and $\nu = 0$. We further provide that in the absence of the external field ($A = 0$) there is such a p^* that the above given condition exactly holds for the forward rate k_f and for the given parameters Ω_0 and E_r, i.e, $p^*\omega_0 = \Omega_0 - E_r/\hbar$. This means that without an external field transitions in the TLS take place with the participation of p^* HB quanta.

Then let us pose the question about the set of external frequencies Ω for which a blocking and inversion effect is possible. For example, it could evidently happen if the condition for Δ holds for the backward rate k_b at $p = p^*$ and $\Omega = 2\Omega_0/l$. Note that the latter condition for the possible observation of the blocking and inversion is confirmed numerically for a finite spectral linewidth (see Fig. 1).

Finally, we note that the fast stochastic fluctuations tend to equilibrate the forward and the backward rate [Fig. 1(b)] and to smear out the effects caused by the oscillating field. This result is intuitively clear since the blocking and inversion effects are especially strong when the energy conservation condition (inequality for Δ) holds exactly. The increase of the jump frequency ν leads generally to the broadening of the spectral line $\Phi_\nu(x)$ and hence tends to smear out the resonances.

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