Dissipative transfer of a quantum particle in a dimer with random fluctuating intersite matrix element

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Kinetic equations of the quantum particle motion in a symmetric dimer are studied for the case of fluctuating site energies and a fluctuating intersite coupling matrix element. Modulations of the site energies are incorporated via quantum fluctuations of a thermal bath whereas the fluctuations of the intersite coupling are taken into account by a stochastic description. In contrast to the quantum fluctuations which are considered in the weak coupling limit, the stochastic fluctuations are included in an exact manner. The exact solution of the averaged kinetic equations are obtained in the case of an Ohmic thermal bath with a white noise spectrum and dichotomous fluctuations of the intersite coupling.

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The transfer of quantum particles, such as electrons, protons, and excitons in molecular systems is a subject of constant interest in chemical physics (see, e.g., [1,2]). Depending on the influence of the medium this transfer may occur in the coherent and incoherent regime [3]. To accommodate the medium effects on the transfer dynamics, two different methods are used. In the first method the medium is modeled as a bath of harmonic oscillators staying in thermal equilibrium. This method relies on the treatment of the Liouville equation for the whole system (quantum particle plus medium degrees of freedom) and the use of an appropriate elimination procedure to obtain the equation of motion for the reduced density matrix of the quantum particle [3–8]. As the second approach, we mention the method where the environment is treated phenomenologically and semiclassically via the introduction of a stochastic term into the Hamiltonian (Haken-Strobl-Reineker model) [3,9–14].

Recently, a complementary approach which combines the advantages of both above methods has been suggested [15–17]. In this approach the medium is considered mainly as a set of quantum harmonic oscillators [thermal bath (TB)]. But with respect to some highly anharmonic and low frequency medium degrees of freedom a stochastic description is utilized. Such an approach is extremely useful if the medium contains mobile atoms or molecular groups. The method has been applied recently to the study of incoherent bridge mode assisted transfer of a quantum particle in a dimer with dichotomically fluctuating site energies [16]. If the transfer of a quantum particle is caused by an interaction with a single damped harmonic oscillator (reaction coordinate) the rate of incoherent transfer may be changed by several orders of magnitude depending on the dichotomical energy fluctuation [16].

In the present paper we consider the transfer of a quantum particle in a symmetric dimer with quantum fluctuating site energies and a dichotomically fluctuating intersite matrix element. The complete Hamiltonian of the system under consideration consists of three terms,

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

The first term,

$$H_0 = E_0 \mid 1\rangle\langle 1 \mid + E_0 \mid 2\rangle\langle 2 \mid + \frac{1}{2} L_0 [\mid 1\rangle\langle 2 \mid + \mid 2\rangle\langle 1 \mid] \ , \tag{2}$$

describes the coherent motion of a quantum particle between the two sites "1" and "2". Here, E_0 is the site energy of the quantum particle in the basis of localized states $\mid 1\rangle$ and $\mid 2\rangle$, and L_0 is the intersite matrix element. The second term in Eq. (1),

$$V(t) = \hat{F}_1 \mid 1\rangle\langle 1 \mid + \hat{F}_2 \mid 2\rangle\langle 2 \mid + \frac{1}{2}\alpha(t)[\mid 1\rangle\langle 2 \mid + \mid 2\rangle\langle 1 \mid] \ , \tag{3}$$

includes fluctuations of the site energies caused by the generalized forces

$$\hat{F}_n = \sum_{\lambda} \kappa_{n\lambda} (\hat{b}^+_{n\lambda} + \hat{b}_{n\lambda}) \ . \tag{4}$$

The TB is modeled by a set of harmonic oscillators (hereafter $\hbar = 1$)

$$H_T = \sum_{n\lambda} \omega_{n\lambda} (\hat{b}^+_{n\lambda} \hat{b}_{n\lambda} + \tfrac{1}{2}) \ . \tag{5}$$

The intersite matrix element fluctuations, $\alpha(t)$, result from the stochastic degrees of freedom of the environment.

In Eqs. (3)–(5) $\omega_{n\lambda}$ is the frequency of the $n\lambda$th bath mode, $\hat{b}^{+}_{n\lambda}$ ($\hat{b}_{n\lambda}$) is the creation (annihilation) operator, $\kappa_{n\lambda}$ is the coupling constant, and $\alpha(t)$ denotes a dichotomous Markov process (DMP). It takes the values $\alpha(t) = \pm\Delta$ with zero mean $\langle\alpha(t)\rangle = 0$ and exponentially decaying autocorrelation function $\langle\alpha(t)\alpha(t')\rangle = \Delta^2 \exp[-\nu(t-t')]$ [18,19]. Δ and ν are the mean square amplitude and reverse autocorrelation time of $\alpha(t)$, respectively. Such a process corresponds, for example, to the thermal activated switching of a charged molecular group or ion between local minima of symmetric bistable potential. Note also that the above choice of the model Hamiltonian supposes statistically independent fluctuations of the sites energies.

To treat the intersite transfer dynamics in the considered problem we have to set up the kinetic equation for the difference $\sigma_z(t) = \gamma_{11}(t) - \gamma_{22}(t)$ of the monomer state populations $\gamma_{nn}(t) = Sp[\hat{\gamma}_{nn}\rho(t)]$ $(n = 1,2)$ and the interstate coherence $\sigma_y(t) = i[\gamma_{12}(t) - \gamma_{21}(t)]$. Here, $\hat{\gamma}_{nn'} = | n\rangle\langle n' |$ is the transition operator and $\rho(t)$ denotes the reduced density matrix of the quantum particle [the notation $\sigma_z(t)$ is used here bearing in mind the correspondence of the considered problem with the so-called spin-boson problem [20]].

Let us consider a situation in which the quantum fluctuations are regarded as weak (the limiting case of a small reorganization energy of the medium) but the intersite matrix element fluctuations may be arbitrary. Then the relevant kinetic equations can be reduced either from the general kinetic equations obtained in [7,16] or from the Argyres and Kelley master equation [17,21] originally derived in the theory of spin resonance and relaxation [22]. Proceeding and using the standard assumption of an initial decoupling of the quantum particle and the TB, one obtains in the second Born approximation with respect to the coupling of the quantum particle and the TB

$$\dot{\sigma}_z(t) = [L_0 + \alpha(t)]\sigma_y(t) ,$$
$$\dot{\sigma}_y(t) = -[L_0 + \alpha(t)]\sigma_z(t) - \int_0^t dt' K_s(t-t')\sigma_y(t') . \quad (6)$$

The symmetrized autocorrelation function

$$K_s(\tau) = \frac{1}{2}[K_1(\tau) + K_2(\tau)] \quad (7)$$

with

$$K_{n=1,2}(\tau) = [\langle \hat{F}_n(\tau)\hat{F}_n(0)\rangle_T + \langle \hat{F}_n(0)\hat{F}_n(\tau)\rangle_T] \quad (8)$$

characterizes the energy fluctuations of the state $|1\rangle$ and $|2\rangle$, respectively. Here, $\hat{F}(\tau) = \exp(iH_T\tau)\hat{F}\exp(-iH_T\tau)$, and $\langle\cdots\rangle_T$ denotes the average over the equilibrium state with temperature T of the TB. It can be simply shown that $\sigma_z(t)$ alone obeys a Langevin-like equation which is formally equivalent to the equation of motion of a harmonic oscillator with frequency-dependent friction and stochastically modulated mass and force coefficient.

Equations (6) can be averaged with respect to the DMP without any approximation in using the Shapiro and Loginov theorem [23]. According to this theorem, any retarded functional, $f(t)$, of the dichotomous process $\alpha(t)$ must obey the following equation:

$$\frac{d}{dt}\langle\alpha(t)f(t)\rangle = -\nu\langle\alpha(t)f(t)\rangle + \left\langle \alpha(t)\frac{d}{dt}f(t)\right\rangle , \quad (9)$$

where $\langle\cdots\rangle$ denotes the average over the DMP. Using Eq. (9) and the remarkable property of the DMP, $\alpha^2(t) = \Delta^2$, we obtain from Eqs. (6) the final set of coupled integro-differential equations. They contain the quantities $\sigma_{z,y}(t)$ averaged with respect to the DMP and the related first moments $\langle\alpha(t)\sigma_{z,y}(t)\rangle$,

$$\frac{d}{dt}\langle\sigma_z(t)\rangle = L_0\langle\sigma_y(t)\rangle + \langle\alpha(t)\sigma_y(t)\rangle ,$$
$$\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\nu\langle\alpha(t)\sigma_z(t)\rangle + L_0\langle\alpha(t)\sigma_y(t)\rangle + \Delta^2\langle\sigma_y(t)\rangle ,$$
$$\frac{d}{dt}\langle\sigma_y(t)\rangle = -L_0\langle\sigma_z(t)\rangle - \langle\alpha(t)\sigma_z(t)\rangle - \int_0^t K_s(t-t')\langle\sigma_y(t')\rangle dt' ,$$
$$\frac{d}{dt}\langle\alpha(t)\sigma_y(t)\rangle = -\nu\langle\alpha(t)\sigma_y(t)\rangle - L_0\langle\alpha(t)\sigma_z(t)\rangle - \Delta^2\langle\sigma_z(t)\rangle - \int_0^t K_s(t-t')\langle\alpha(t)\sigma_y(t')\rangle dt'. \quad (10)$$

We chose the initial conditions as $\langle\alpha(0)\sigma_{z,y}(0)\rangle = 0$, $\langle\sigma_z(0)\rangle = n_0$, and $\langle\sigma_y(0)\rangle = m_0$. Equations (10) are the relevant kinetic equations we are interested in.

Their further analysis requires the knowledge of the correlation function $K_s(\tau)$ which is determined by the spectral density

$$J_n(\omega) = 2\pi\sum_{\lambda}\kappa^2_{n,\lambda}[\delta(\omega-\omega_{n,\lambda}) - \delta(\omega+\omega_{n,\lambda})] . \quad (11)$$

Here, we take a high-temperature limit and the classical description of the TB with white noise spectrum $J(\omega) = \eta\omega$ [24,25], such that

$$K_s(\tau) = \eta k_B T\delta(\tau) . \quad (12)$$

This high-temperature approximation is appropriate whenever the bandwidth of the medium degrees of freedom is much larger than the intrasite matrix element [3,11]. The choice of the correlator $K_s(\tau)$ in the form (12) corresponds to the generalization of the Haken-Strobl-Reineker (HSR) model [3,11] to the case of a dichotomically fluctuating intersite matrix element. It can be treated as a basic approximation bearing in mind the possibility of its subsequent generalization. Therefore, we restrict ourselves to the case of Eq. (12). Equation (10) can be solved exactly using the Laplace-transform method. Providing an initial localization of the quantum particle at site "1", i.e., $\langle\sigma_z(0)\rangle = 1$, $\langle\sigma_y(0)\rangle = 0$, the solution of the set of Eqs. (10) follows as

$$\langle\sigma_z(t)\rangle = \sum_{s=1}^{4} \frac{A(p_s)}{B'(p_s)} e^{p_s t} . \tag{13}$$

This expression contains

$$\begin{aligned} A(p) &= p^3 + 2(\nu+\xi)p^2 + (3\xi\nu + \xi^2 + \nu^2 + L_0^2 + \Delta^2)p + \nu^2\xi + \Delta^2\nu + \Delta^2\xi + \nu\xi^2 + L_0^2\xi , \\ B(p) &= p^4 + 2(\nu+\xi)p^3 + (\xi^2 + 2\Delta^2 + 2L_0^2 + 3\xi\nu + \nu^2)p^2 + (\nu^2\xi + 2\Delta^2\xi + 2L_0^2\nu + 2\Delta^2\nu + 2L_0^2\xi + \nu\xi^2)p \\ &\quad + L_0^2\nu\xi + \Delta^2\nu\xi + L_0^2\nu^2 - 2L_0^2\Delta^2 + L_0^4 + \Delta^4 , \\ B'(p) &= dB(p)\,/\,dp , \end{aligned} \tag{14}$$

and

$$\begin{aligned} p_{1,2} &= -\frac{\nu}{2} - \frac{\xi}{2} \pm \frac{\sqrt{\nu^2 + \xi^2 + 2\sqrt{\xi^2\nu^2 - 4L_0^2\nu^2 + 16L_0^2\Delta^2} - 4\Delta^2 - 4L_0^2}}{2} , \\ p_{3,4} &= -\frac{\nu}{2} - \frac{\xi}{2} \pm \frac{\sqrt{\nu^2 + \xi^2 - 2\sqrt{\xi^2\nu^2 - 4L_0^2\nu^2 + 16L_0^2\Delta^2} - 4\Delta^2 - 4L_0^2}}{2} \end{aligned} \tag{15}$$

are the roots of the equation $B(p) = 0$. Here we denote

$$\xi = \eta k_B T . \tag{16}$$

In the limiting case $\nu, \Delta \to \infty$, $f = \Delta^2/\nu = \text{const}$, which corresponds to the δ-correlated fluctuations of the intersite matrix element with strength f, we get from Eq. (15)

$$p_{1,3} = -f - \frac{\xi}{2} \pm \frac{\sqrt{\xi^2 - 4L_0^2}}{2}, \quad p_{2,4} \to -\infty . \tag{17}$$

Hence, in the above limit our model correlates with the HSR model [3,11] with the transition rates $\lambda_{1,2} = -p_{1,3}$ and the parametrization: $\gamma_0 = \xi/2$, $J = L_0/2$, $\gamma_1 = \bar{\gamma}_1 = f/4$. It reproduces the well-known criterion of the transition from coherent to incoherent transfer [11]

$$\xi \geq \xi_c = 2L_0 . \tag{18}$$

This inequality means that in the case of $\xi < \xi_c$ the averaged state populations $\langle\gamma_{11}(t)\rangle = [1 + \langle\sigma_z(t)\rangle]/2$ and $\langle\gamma_{22}(t)\rangle = [1 - \langle\sigma_z(t)\rangle]/2$ approach their steady-state value $\gamma_{11} = \gamma_{22} = 1/2$ by damped oscillations (coherent transfer). On the other hand, for $\xi \geq \xi_c$, the transfer rates are real and the averaged state populations reach their steady-state values without oscillations (incoherent transfer).

It is necessary to stress that in contrast to the more involved generalization of the HSR model [14], our model allows an analytical treatment and thus reveals peculiarities [26]. We get the expressions for the transition rates $\lambda_s = -p_s$ in the rather simple analytical form (15) for arbitrary amplitude Δ and frequency ν of the intersite matrix element fluctuations where the situation is generally more involved. If the Kubo number [27] of the DMP, $K = \Delta/\nu$, is less than

$$K_c = \frac{1}{2\sqrt{1 + 4L_0^2/\nu^2}} < \frac{1}{2} , \tag{19}$$

then the criterion Eq. (18) is modified as

$$\xi \geq \xi_c = 2L_0\sqrt{1 - 4K^2} . \tag{20}$$

As can be seen from Eq. (20) the colored dichotomous noise reduces the transition temperature which corresponds to the parameter ξ_c. Note that by virtue of the fact that at $K \to 0$, the dichotomous noise has the Gaussian-like limit (i.e., it can be considered as a pre-Gaussian noise [28]), one can expect that the similar criterion (20) will also be valid for the weakly colored Gaussian noise ($K \ll 1$). Note also that in the case $K < K_c$, for the parameter ξ being in the range

$$\xi_c < \xi_1 < \xi < \xi_2 , \tag{21}$$

where $\xi_{1,2} = \sqrt{4L_0^2 + \nu^2} \mp 2\Delta$, the transition rates $\lambda_{3,4}$ have complex values again. However, the numerical examination shows that the coefficients corresponding to p_3 and p_4 in the expansion (13) are small in this case and, therefore, the transfer remains incoherent.

In the case of strongly colored noise and $K > K_c$, all four roots (15) are complex if $\xi < \xi_1$, i.e., $p_1 = p_2^*$, $p_3 = p_4^*$, and thus the transfer of the quantum particle occurs in the coherent regime. A more complicated situation appears in the intermediate range (21). In this case there are two real roots, p_1 and p_2, and two complex conjugated roots, p_3 and $p_4 = p_3^*$. Therefore, depending on the relation between Δ, ν, and L_0, the three regimes (coherent, incoherent, and a combined one) are possible (see also [26,29]). An example for such a combined regime is given in Fig. 1(a) for the special case $\Delta = L_0$, which corresponds to a situation where the coherent transfer

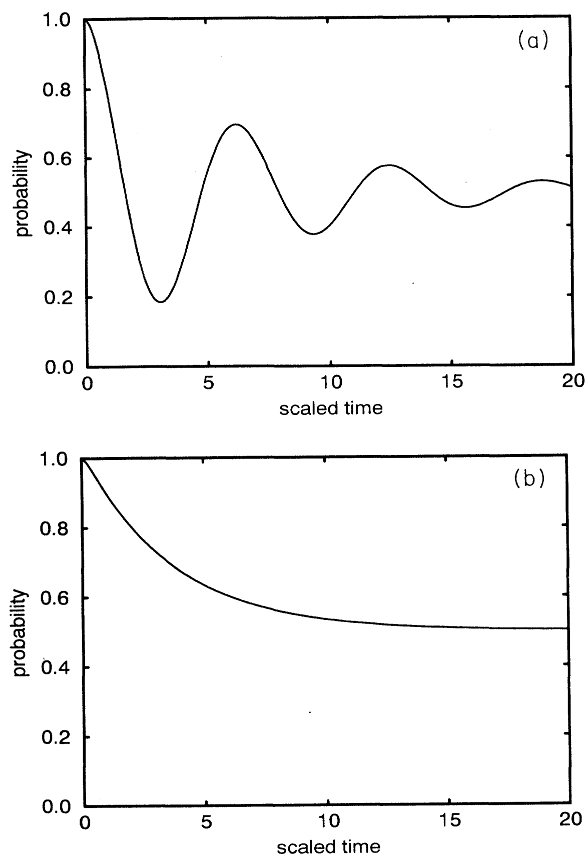

FIG. 1. Dependence of $\langle\gamma_{11}\rangle$ on time t (in units of L_0^{-1}) for different values ξ with $\Delta = L_0$ and $\nu = 0.1L_0$: (a) $\xi = 0.5L_0$, (b) $\xi = 5L_0$.

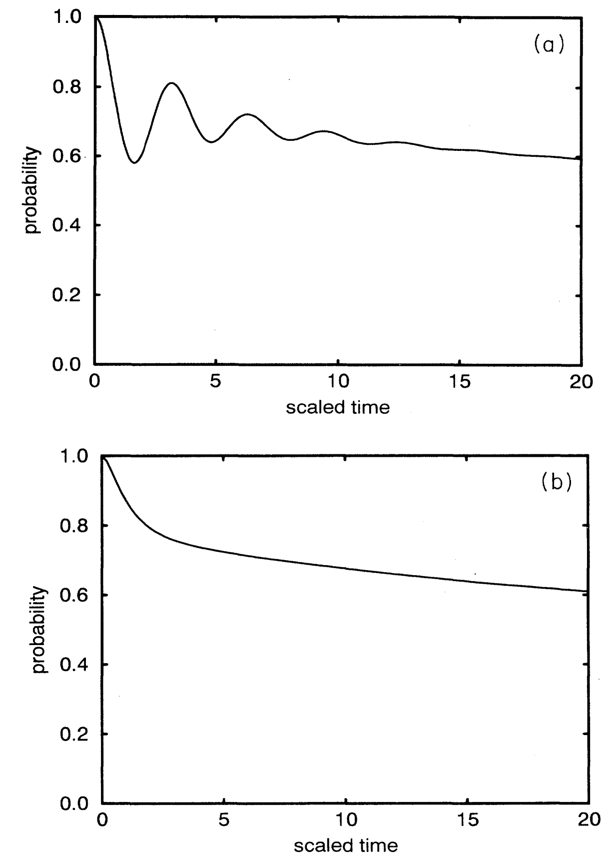

FIG. 2. Dependence of $\langle\gamma_{11}\rangle$ on time t (in units of L_0^{-1}) for different values ξ with $\Delta = L_0$ and $\nu = 10L_0$: (a) $\xi = 0.1L_0$, (b) $\xi = 5L_0$.

is stochastically interrupted. It is seen from Fig. 1(a) that in the case of slow fluctuation of $\alpha(t)$ ($\nu << L_0$) there are two stages of the transfer process. The first stage is characterized by the damped coherent oscillations, and the second one reflects an incoherent behavior occurring on the essentially different time scale. This combined regime is transformed into the two-stage incoherent relaxation [Fig. 1(b)], when $\xi > \xi_2$. Note that in both cases a long-time behavior of the averaged state populations is completely driven by the fluctuations of the intersite matrix element, $\alpha(t)$, independently of the parameter ξ, and has the incoherent character with transition rate $\lambda_1 \approx \nu/2$ (Fig. 1). In this case the temperature dependence of the transition rate λ_1 must have an exponential character according to the Arrhenius law, $\lambda_1 \sim \exp(-\beta V_0)$, where V_0 is the barrier height of the above bistable potential. In the reverse case of fast fluctuations of $\alpha(t)$ ($\nu >> L_0$), the long-time behavior of the averaged state populations $\langle\gamma_{nn}(t)\rangle$ is mainly determined by the dissipation processes in the thermal bath. The decay of the averaged state populations occurs much faster (Fig. 2). In the coherent regime the rate of this decay grows linearly with temperature according to Eqs. (15) in contrast to the case of slow fluctuations.

In summary, it can be stated that the interplay of the dichotomic fluctuations of the intersite matrix element and the dissipative processes in the thermal bath can essentially modify the transfer dynamics of a quantum particle in symmetric dimer. In the present paper we have examined this problem for the case of an Ohmic thermal bath with white noise spectrum, where an analytical treatment is possible. In particular, it was shown that the weakly colored noise reduces the transition temperature from the coherent regime to the incoherent one according to Eq. (20). Furthermore, it could be demonstrated that the strongly colored noise causes additional features in the transfer dynamics. The appearance of a combined regime [Fig. 1(a)] and the feature in the temperature dependence of the transfer rate has been discussed. Note that the introduction of a finite correlation time of the thermal bath and the inclusion of low-temperature corrections is possible in the present model. The corresponding work is in progress.

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