Combined influence of random and regular external fields on long-range electron transfer

I. A. Goychuk and E. G. Petrov
Bogolyubov Institute for Theoretical Physics, Ukrainian National Academy of Science, 14-b Metrologichna Street, 252143 Kiev, Ukraine

V. May
Institut für Physik, Humboldt-Universität zu Berlin, Hausvogteiplatz 5-7, D-10117 Berlin, Germany
(Received 3 January 1997; revised manuscript received 4 April 1997)

The dissipative dynamics of a two-level system (TLS) is studied for the case of the simultaneous modulation of the energy bias by a regular external field and by nonequilibrium dichotomic fluctuations. To describe the noise-averaged dynamics driven by the external periodic field, a set of coupled generalized master equations is derived. Quantum fluctuations of the thermal bath are taken into account within the noninteracting blip approximation, whereas the dichotomic fluctuations and the external field are treated in an exact manner. The case of nonadiabatic continuous-wave (cw) driving is considered in detail for an asymmetric TLS strongly coupled to the thermal bath. The general approach is applied to long-range electron transfer in proteins. According to the presence of dynamic disorder, the coarse-grained electron transfer dynamics becomes nonexponential. The gated regime and the inversion effect of the transfer in the strongly biased TLS with a dichotomic fluctuating energy bias are demonstrated. Additionally, it is shown that a strong cw field can switch the electron transfer dynamics between the gated (nonexponential) regime and the nonadiabatic (single-exponential) regime. [S1063-651X(97)13007-0]

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

I. INTRODUCTION

Cooperative effects stemming from the combined action of periodic or random external forces on dissipative quantum dynamics are the subject of increasing interest in different fields of physics [1–15]. The principal attention was paid to the driven spin-boson model or, in other terms, to the driven dissipative two-level system (TLS). Besides its fundamental importance [16–18], this model has a number of applications ranging from tunneling of defects in solids and magnetic flux dynamics in superconducting quantum interference devices at low temperatures [1,2,5,6,15–17] to electron transfer (ET) reactions in solvents [7] and proteins [19,10–12]. Both, the averaged transient dynamics as well as the steady-state behavior of the driven spin-boson model gained essential interest. It was shown, for example, that one can strongly suppress or enhance the ET rates by means of strong periodic fields [6,7,12]. The suppression [4,6] or, vice versa, the induction [20] of coherence effects in the dissipative tunneling dynamics could be also demonstrated. Furthermore, the behavior of the time-averaged steady state can essentially deviate from the time-independent case. It was shown that the application of a regular external field can change the ratio of the steady-state level occupations in a TLS by many orders of magnitude [2,7,12]. Moreover, this ratio can even be inverted. In an application to long-range ET in proteins, this means that one can externally invert the transfer direction. Besides these examples, the interest in full (nonaveraged) response of a damped quantum system to a periodic external perturbation originated in the field of the quantum stochastic resonance (see, e.g., Ref. [20] and references therein).

Combining the action of periodic and random external fields on dissipative quantum dynamics, one obtains a number of interesting effects [21]. In particular, such effects are of interest in the context of electron and energy transduction processes in biology, where random fields can be created by nonequilibrium degrees of freedom of the complex molecular structure (see, e.g., Ref. [22] for general discussions). Such random fields should rather be considered dynamic (or energy-driven) noises than thermal ones [13,23]. Nonequilibrium effects produced by such noises (directional diffusion of a Brownian particle in ratchets, noise-driven molecular motors, etc.) are currently under discussion in the field of classical physics (see, e.g., Ref. [24] and further references therein). However, they can also begin to be explored for quantum systems, for which one example will be given below.

The additional inclusion of a periodic external field provides a further possibility to regulate the transfer process in complex molecular systems. It is the aim of the present paper to study such a possibility for the driven spin-boson model with dichotomically and periodically modulated energy bias. We apply this model to the long-range ET in a protein which fluctuates between two conformations. Such a transfer basically involves two (donor and acceptor) electronic states $|1\rangle$ and $|2\rangle$, separated by a large distance $r > 10$ Å. At such distances the direct overlap of donor and acceptor electronic wave functions is negligible, and the transfer must also occur with the participation of intermediate electronic states. If these states lie high in energy, they are not practically populated during the transfer process, and their role reduces to providing effective electronic coupling between the donor and the acceptor. A similar transfer mechanism is usually referred to as superexchange [25,26]. In such a case, the long-range ET can be described within the effective dissipative two-level model or within the equivalent spin-boson model [19]. Furthermore, suppose that the transfer of an electron from donor to acceptor, $DA \to D^+A^-$, creates the

1063-651X/97/56(2)/1421(8)/$10.00

ion pair $D^{+}A^{-}$ and the associated dipole moment $d=er$ [26]. Then the external electric field $\mathcal{E}(t)$ can produce an additional time-dependent bias $\Delta\varepsilon(t)=d\mathcal{E}(t)$ between the donor and acceptor energy levels. Since the amplitude of this bias is directly proportional to the transfer distance, the long-range ET is the preferable type of ET to realize the theoretical predictions of Refs. [7,12] on the possible field effects. Note, however, that the parameters of the effective two-level model can undergo additional fluctuations according to the protein jumplike conformational dynamics. Accordingly, either the effective electronic coupling or the energy bias can be randomly modulated [27]. Recently the first possibility was studied in Ref. [21]. In the present work we proceed with its alternative.

The paper is organized as follows. In Sec. II we briefly consider the extension of the familiar spin-boson model to the case where the energy bias undergoes random jumps between two values and is additionally modulated by an external force. Then, a set of noise-averaged generalized master equations obtained in the noninteracting blip approximation (NIBA) will be presented. The case of nonadiabatic cw driving is treated in Sec. III within the Markov approximation. In Sec. IV the general model is specified to the problem of long-range ET in proteins. The obtained results and concluding remarks form Sec. V.

II. DRIVEN SPIN-BOSON MODEL WITH ENERGETIC DISORDER

We start with the well-known spin-boson model [16,17], including a time-dependent energy bias in the following Hamiltonian:

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

Here, $\hat{\sigma}_z=|1\rangle\langle 1|-|2\rangle\langle 2|$ and $\hat{\sigma}_x=|1\rangle\langle 2|+|2\rangle\langle 1|$ are the pseudospin operators defined by two localized states $|1\rangle$ and $|2\rangle$. These states are coupled by the tunneling matrix element V. The energy difference of the localized states (or the energy bias) $\varepsilon(t)=E_1(t)-E_2(t)$ is taken as an explicitly time-dependent quantity. The thermal bath is supposed to be harmonic, with b_{λ} and $b_{\lambda}^{\dagger}$ as the bath quanta annihilation and creation operators, respectively. Its stochastic influence is represented by a time-dependent operator $\hat{F}(t)=\hbar^{-1}\Sigma_{\lambda}\kappa_{\lambda}(b_{\lambda}^{\dagger}e^{i\omega_{\lambda}t}+b_{\lambda}e^{-i\omega_{\lambda}t})$, with the nonvanishing second moment $K(t)=\langle\hat{F}(t)\hat{F}(0)\rangle_T=\int_0^{\infty}J(\omega)[\coth(\hbar\omega/2k_BT)\cos(\omega t)-i\sin(\omega t)]d\omega$ [16,17]. Here $J(\omega)=\hbar^{-2}\Sigma_{\lambda}\kappa_{\lambda}^2\delta(\omega-\omega_{\lambda})$ is the bath spectral function, and the brackets $\langle\ \rangle_T=\mathrm{Tr}_B(\rho_B\ldots)$ denote the thermal average over the bath with the equilibrium density matrix ρ_B and the temperature T.

The driven spin-boson model Eq. (1) has been the subject of a number of recent studies [1–3,5–7,10–12,21]. In these studies the corresponding NIBA master equation was derived to describe the time evolution of the population difference, $\sigma_z(t)=\mathrm{Tr}_{S+B}(\rho(t)\hat{\sigma}_z)$, where $\rho(t)$ is the density matrix of the full system. We denote this NIBA master equation as [3,5,6,11]

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

where we had shortened

$$\begin{aligned}
f(t,t')&=f_0(t-t')\cos\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right),\\
g(t,t')&=g_0(t-t')\sin\left(\frac{1}{\hbar}\int_{t'}^{t}\varepsilon(\tau)d\tau\right),\\
f_0(t)&=\frac{4V^2}{\hbar^2}\exp[-G_s(t)]\cos[G_a(t)],\\
g_0(t)&=\frac{4V^2}{\hbar^2}\exp[-G_s(t)]\sin[G_a(t)].
\end{aligned} \tag{3}$$

The bath influence function in Eq. (3), $G(t)=G_s(t)+iG_a(t)$, corresponds to that introduced by Leggett *et al.* [16]. Carrying out a double time-integration of the second moment $K(t)$, and taking notice of the expression for the bath reorganization energy, $E_r=\hbar\int_0^{\infty}[J(\omega)/\omega]d\omega$, one obtains $G(t)=\int_0^t dt_1\int_0^{t_1}K(t_2)dt_2+i(E_r/\hbar)t$ [11].

Equation (2) is our starting point for the subsequent consideration. Until this point the time dependence of $\varepsilon(t)$ was not specified, and could be quite arbitrary. Let us consider a model in which $\varepsilon(t)$ undergoes random jumps between two different values. These two values should have equal probabilities to appear, and the jump process should be a dichotomic Markov process (DMP) [28]. Additionally, we suppose that the energy bias can be driven by a regular time-dependent external force, i.e., we assume

$$\varepsilon(t)=\hbar\Delta\alpha(t)+\tilde{\varepsilon}(t), \tag{4}$$

where $\hbar\Delta$ is the amplitude of the jumps, $\alpha(t)$ specifies the DMP, and $\tilde{\varepsilon}(t)$ is a still arbitrary time-dependent part of $\varepsilon(t)$ which *does not correlate* with the dichotomic jump processes. The mean energy bias ε_0 is included in the definition of $\tilde{\varepsilon}(t)$. According to the chosen model we have $\alpha(t)=\pm 1$ with a zero mean, $\langle\alpha(t)\rangle=0$, and, with an exponentially decaying autocorrelation function $\langle\alpha(t)\alpha(t')\rangle=\exp[-\nu|t-t'|]$ [28].

Now, Eq. (2) appears as a stochastic integrodifferential equation which has to be averaged with respect to the possible realizations of $\alpha(t)$. First, one has to decouple the noise average $\langle f(t,t')\sigma_z(t')\rangle$, which can be done using the results of Bourret, Frisch, and Pouquet [29]. In accord with Refs. [11,30], we have $\langle f(t,t')\sigma_z(t')\rangle=\langle f(t,t')\rangle\langle\sigma_z(t')\rangle+\langle f(t,t')\alpha(t')\rangle\langle\alpha(t')\sigma_z(t')\rangle$ *independently* of an additional time dependence of $\tilde{\varepsilon}(t)$. Then it is necessary to obtain an additional equation for the correlator $\langle\alpha(t')\sigma_z(t')\rangle$. Here the theorem of Shapiro and Loginov

[31] can be used. Following, furthermore, in line with the derivation of Ref. [11], we obtain the noise-averaged NIBA master equations

$$\frac{d}{dt}\langle\sigma_z(t)\rangle = -\int_0^t \{F_0(t,t')\langle\sigma_z(t')\rangle - F_1(t,t')\langle\alpha(t')\sigma_z(t')\rangle + G_0(t,t')\}dt',$$

$$\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\nu\langle\alpha(t)\sigma_z(t)\rangle - \int_0^t \{F_2(t,t') \times\langle\alpha(t')\sigma_z(t')\rangle - F_1(t,t')\langle\sigma_z(t')\rangle + G_1(t,t')\}dt'. \tag{5}$$

The various kernels read

$$F_{0,2}(t,t') = S_{0,2}(t-t')f_0(t-t')\cos\left(\frac{1}{\hbar}\int_{t'}^t \tilde{\varepsilon}(\tau)d\tau\right),$$

$$F_1(t,t') = |S_1(t-t')|f_0(t-t')\sin\left(\frac{1}{\hbar}\int_{t'}^t \tilde{\varepsilon}(\tau)d\tau\right), \tag{6}$$

$$G_0(t,t') = S_0(t-t')g_0(t-t')\sin\left(\frac{1}{\hbar}\int_{t'}^t \tilde{\varepsilon}(\tau)d\tau\right),$$

$$G_1(t,t') = |S_1(t-t')|g_0(t-t')\cos\left(\frac{1}{\hbar}\int_{t'}^t \tilde{\varepsilon}(\tau)d\tau\right),$$

where $S_k(\tau) = (i/\Delta)^k(d^k/d\tau^k)S(\tau)$, and

$$S(\tau) = \langle e^{i\Delta\int_{t'}^t \alpha(t')dt'}\rangle = e^{-(\nu/2)\tau}\{\cosh(\tau\sqrt{\nu^2/4-\Delta^2}) + \nu/\sqrt{\nu^2-4\Delta^2}\sinh(\tau\sqrt{\nu^2/4-\Delta^2})\}$$

is the noise-averaged propagator [11] of the celebrated Kubo oscillator [28,32]. Since the present set of equations includes an additional regular time dependence of the bias, it generalizes our earlier derivations of Ref. [11].

III. AVERAGED DYNAMICS AND NONADIABATIC cw DRIVING: MARKOV APPROXIMATION

Now let us specify the type of external driving considered in the remainder of this paper. We restrict ourselves to the simplest case of sinusoidal driving and put $\tilde{\varepsilon}(t) = \hbar\omega_0 + \hbar A\cos(\Omega t)$, where $\hbar\omega_0$ is the constant bias, and $\hbar A$ and Ω are the amplitude and the frequency of periodic driving, respectively. Moreover, we will consider the time-averaged dynamics for the important case of nonadiabatic driving when $\Omega \gg \nu,\Gamma$. Here Γ stands for an effective transient rate which will be defined below. Following the reasoning of Refs. [2] or [12], one can show that the averaged dynamics obeys the averaged equations which are similar to Eqs. (5), but formulated with the kernels which have been averaged with respect to the oscillations period according to the rule $\overline{f(t+\tau,t)} = (\Omega/2\pi)\int_0^{2\pi/\Omega}dt\, f(t+\tau,t)$. This averaging can be easily carried out by noting the well-known relation $\exp(i\zeta\omega t) = \sum_{p=-\infty}^{\infty}J_p(\zeta)\exp(ip\omega t)$. Here $J_p(\zeta)$ is the Bessel function of the first kind, and we have to identify in the present case $\zeta = A/\Omega$.

Let us perform such an averaging procedure, and, afterward, consider a situation where the decay time τ_d defined by the function $G_s(t)$ is very small in comparison to the relaxation time Γ^{-1}, i.e., $\Gamma\tau_d \ll 1$. Then one can perform the Markov approximation with respect to the *averaged* equations (and not before), and the following set of equations of motion describing the averaged incoherent dynamics is obtained:

$$\frac{d}{dt}\overline{\langle\sigma_z(t)\rangle} = -k_0\overline{\langle\sigma_z(t)\rangle} + k_1\overline{\langle\alpha(t)\sigma_z(t)\rangle} - c_0,$$

$$\frac{d}{dt}\overline{\langle\alpha(t)\sigma_z(t)\rangle} = k_1\overline{\langle\sigma_z(t)\rangle} - (\nu+k_2)\overline{\langle\alpha(t)\sigma_z(t)\rangle} - c_1. \tag{7}$$

The coefficients k_0, k_1, and k_2, are given by

$$k_i = \sum_{p=-\infty}^{\infty} J_p^2(\zeta)k_{ip}\ , \tag{8}$$

and in a similar manner we express c_0 and c_1. The expansion coefficients correspond to a similar problem without the periodic driving, and to the shifted mean energy gap $\tilde{\varepsilon} = \hbar\omega_p = \hbar(\omega_0 + p\Omega)$. They read as

$$k_{0,2p} = \frac{4V^2}{\hbar^2}\int_0^\infty e^{-G_s(\tau)-(\nu/2)\tau}\left\{\cosh(\tau\sqrt{\nu^2/4-\Delta^2}) \pm \frac{\nu}{\sqrt{\nu^2-4\Delta^2}}\sinh(\tau\sqrt{\nu^2/4-\Delta^2})\right\} \times\cos[G_a(\tau)]\cos(\omega_p\tau)d\tau,$$

$$k_{1p} = \frac{4V^2}{\hbar^2}\frac{2\Delta}{\sqrt{\nu^2-4\Delta^2}}\int_0^\infty e^{-G_s(\tau)-(\nu/2)\tau} \times\sinh(\tau\sqrt{\nu^2/4-\Delta^2})\cos[G_a(\tau)]\sin(\omega_p\tau)d\tau, \tag{9}$$

$$c_{0p} = \frac{4V^2}{\hbar^2}\int_0^\infty e^{-G_s(\tau)-(\nu/2)\tau}\left\{\cosh(\tau\sqrt{\nu^2/4-\Delta^2}) + \frac{\nu}{\sqrt{\nu^2-4\Delta^2}}\sinh(\tau\sqrt{\nu^2/4-\Delta^2})\right\} \times\sin[G_a(\tau)]\sin(\omega_p\tau)d\tau,$$

$$c_{1p} = \frac{4V^2}{\hbar^2}\frac{2\Delta}{\sqrt{\nu^2-4\Delta^2}}\int_0^\infty e^{-G_s(\tau)-(\nu/2)\tau} \times\sinh(\tau\sqrt{\nu^2/4-\Delta^2})\sin[G_a(\tau)]\cos(\omega_p\tau)d\tau.$$

These expressions are valid in the case $\nu \neq 2\Delta$. To obtain the coefficients in the case $\nu = 2\Delta$, one has to perform the limit $\nu \to 2\Delta$ which is easily achieved.

Equation (7) describes the two-exponential transient dynamics which approaches the steady state

$$\sigma_z^s = -\frac{c_1 k_1 + c_0(\nu + k_2)}{(\nu + k_2)k_0 - k_1^2} \tag{10}$$

of $\overline{\langle \sigma_z(t) \rangle}$ with the rates $\lambda_{1,2} = \frac{1}{2}\{\nu + k_0 + k_2 \pm \sqrt{(\nu + k_2 - k_0)^2 + 4k_1^2}\}$. The smaller rate can be considered as the long-time rate constant $\Gamma_\infty = \lambda_2$. Alternatively, this transient dynamics can be described by the effective transient rate Γ defined as $\Gamma = 1/\langle \tau \rangle$, where

$$\langle \tau \rangle = \frac{\int_0^\infty [\overline{\langle \sigma_z(t) \rangle} - \sigma_z^s] dt}{\sigma_z(0) - \sigma_z^s} \tag{11}$$

is the mean relaxation time (MRT) [33]. Then, in accordance with Eqs. (7) and (11) we get

$$\Gamma = k_0 - \frac{k_1^2}{\nu + k_2}. \tag{12}$$

Furthermore, to have a measure for the deviation of the averaged transient dynamics from the exponential behavior, we introduce the quantity $\chi = 2(\Gamma - \Gamma_\infty)/\Gamma$, which varies between $\chi = 0$ (for the pure exponential relaxation) and $\chi = 1$ (for strong deviations from the single-exponential behavior).

In the absence of any random or periodic driving it follows $\sigma_z^s = -\tanh(\varepsilon_0/2k_B T)$ [16]. Therefore, the ratio of the steady-state level populations, $p_1^s = (1 + \sigma_z^s)/2$ and $p_2^s = (1 - \sigma_z^s)/2$, corresponds to the Boltzmann equilibrium distribution, i.e., $p_1^s/p_2^s = \exp(-\varepsilon_0/k_B T)$. Strong external driving leads to the deviation from the equilibrium distribution, which can be accounted for by the effective energy bias introduced as $\varepsilon_{\text{eff}} = k_B T \ln(p_2^s/p_1^s)$. Similar effects have been already discussed for the cases of random and periodic driving apart [2,7,10–12], and for the combined action of a dichotomic fluctuating intersite coupling and a periodically fluctuating energy bias [21].

Next let us discuss some general properties of the averaged dynamics stemming from Eqs. (7), (8), and (9). In the case of degenerated TLS's, i.e., $\varepsilon_0 = 0$, we have $k_1 = 0$. Thus the dynamics is single exponential with the transfer rate $\Gamma = k_0$ independent on the amplitude Δ and the frequency ν of the energy bias fluctuations, as well as independent on the amplitude A and frequency Ω of the periodic driving. This result is similar to the case of a minor periodic driving [11]. Furthermore, in the case of a small Kubo number, $K = \Delta/\nu \ll 1$ [28], we have $k_1 \ll k_0, k_2$. Hence it follows that $\Gamma \approx \Gamma_\infty \approx k_0$, and single-exponential averaged dynamics is also obtained in this case.

The extreme case of large Kubo numbers, $K \gg 1$, is of more interest. Now, if fluctuations are very slow with respect to the decay time τ_d, i.e., $\nu \tau_d \ll 1$, we have

$$k_{0p} \approx k_{2p} \approx \tfrac{1}{2}(k_p^+ + k_p^-), \quad k_{1p} \approx \tfrac{1}{2}(k_p^- - k_p^+),$$
$$c_{0p} \approx \tfrac{1}{2}(c_p^+ + c_p^-), \quad c_{1p} \approx \tfrac{1}{2}(c_p^+ - c_p^-) \tag{13}$$

as a first-order approximation. Here the quantities

$$k_p^\pm = \frac{4V^2}{\hbar^2}\int_0^\infty e^{-G_s(\tau)} \cos[G_a(\tau)] \cos[(\omega_p \pm \Delta)\tau] d\tau,$$
$$c_p^\pm = \frac{4V^2}{\hbar^2}\int_0^\infty e^{-G_s(\tau)} \sin[G_a(\tau)] \sin[(\omega_p \pm \Delta)\tau] d\tau \tag{14}$$

correspond to a situation with static dichotomic disorder, i.e., $\varepsilon(t) = \varepsilon_0 \pm \hbar\Delta + \hbar A \cos(\Omega t)$.

Note that one can obtain Eq. (7) with the coefficients specified by Eqs. (8), (13), and (14) directly from Eq. (2) in three steps. First, one has to introduce the Markov approximation directly in Eq. (2). Then it is necessary to perform the averaging over fast nonadiabatic oscillations of the energy bias in the resulting differential equation, and to assume the *adiabatic* dependence of the coefficients on the dichotomic fluctuations. After this, one has to average the resulting stochastic differential equation over the *dichotomically fluctuating coefficients*. Such an approximation disregards the interference of the quantum fluctuations of the heat bath and of the random external driving. Mathematically this is expressed by the absence of the term $\nu\tau/2$ in the exponent of expressions (14), which can badly modify the dependence of k_{ip} on ω_p at large ω_p [11,21]. Nevertheless, this approximation is very useful for the qualitative analysis.

Such an analysis of the rate expression (12) for fluctuations with a large Kubo number shows that $\Gamma \approx \nu$, if the inequality

$$\frac{2k^+k^-}{k^+ + k^-} \ll \nu \ll \tfrac{1}{2}(k^+ + k^-) \tag{15}$$

is fulfilled, where $k^\pm = \sum_{p=-\infty}^{\infty} J_p^2(\zeta) k_p^\pm$. It is easy to guarantee this condition when k^+ and k^- differ largely from one another, i.e., $k^- \gg k^+$. Then inequality (15) simplifies to $2k^+ \ll \nu \ll k^-/2$, and the effective transient rate is defined exclusively by the rate of dichotomic jumps, or, in other words, is gated by these jumps. A similar regime was also revealed for the model of dichotomically interrupted intersite coupling [10]. It is worth mentioning that the discussed strong inequality can be either destroyed or improved by the periodic field which can essentially modify the rates $k^\pm$. This offers a way to switch the averaged transient dynamics between different regimes.

IV. PERIODICALLY DRIVEN LONG-RANGE ELECTRON TRANSFER WITH DYNAMIC DISORDER

To illustrate the approach, we consider a long-range ET in proteins. We identify the energy ε_0 of the spin-boson model with the free-energy gap E_g. $\hbar\Delta$ corresponds to the amplitude of fluctuations of the free-energy gap between $E_g^+ = E_g + \hbar\Delta$ and $E_g^- = E_g - \hbar\Delta$. These nonequilibrium fluctuations are supposed to result from jumps of the macromolecule between two conformations with equal probability. Such jump processes could be inherent to complex electron transferring molecular structures (see an example in Ref. [34]). In addition, they can be stimulated, e.g., by the dichotomic fluctuations of the transmembrane potential $\Delta\varphi(t)$ via the mechanism of electroconformational coupling. This could happen, for example, if the considered protein is located in a biological membrane, and realizes ET from one side of membrane to the other [22]. Such fluctuations of the electric potential can be also directly coupled to the dipole moment $\vec{d} = e\vec{r}$. Clearly, dichotomic fluctuations of the energy bias can also be induced by an externally applied random electric field. In any case, these fluctuations have to occur in an *autonomous* regime to justify the applied *external* noise model. Additionally, the regular electric field $\vec{\mathcal{E}}(t)=\vec{\mathcal{E}}_0\cos(\Omega t)$, which should be applied parallel to the dipole moment $\vec{d}$, results in the free-energy gap oscillations with the amplitude $\hbar A=|\vec{d}|\cdot|\vec{\mathcal{E}}_0|$. Note that a time-independent external electric field can be introduced in the definition of E_g as an additional energy shift.

To derive the ET rate it is supposed that the electron couples to a dense set of the low-frequency protein vibrations with upper cutoff frequency ω_D. (In proteins, ω_D is typically about 30 cm^{-1} [25]). If room-temperature conditions $k_BT \gg \hbar\omega_D$ are provided, one can consider the influence of the protein vibrations on the ET in the quasiclassical approximation, and approximate $\coth(\hbar\omega/2k_BT)\approx 2k_BT/\hbar\omega$ in the expression for $K(t)$. Then the mean-square amplitude of the energy gap fluctuations caused by vibrations is $\hbar\Delta_T=\hbar\sqrt{K(0)}\approx\sqrt{2E_rk_BT}$ *independently* of any concrete model of $J(\omega)$. Here E_r is the reorganization energy of low-frequency vibrations which can be treated now as a phenomenological parameter. Furthermore, we assume that the reorganization energy is large enough to ensure the strong inequality $\sqrt{2E_rk_BT}\gg\hbar\omega_D$. Then one can use the short-time approximation of the bath influence function $G(t)$, i.e., $G(t)\approx k_BTE_rt^2/\hbar^2+iE_rt/\hbar$ [19]. Substituting this expression into Eq. (9), one can express the related integrals via the error function of a complex variable similar to that done in Refs. [11,21]. Then Eqs. (8), (10), and (12) can easily be calculated numerically.

To demonstrate the possible effects of the combined action of the dichotomic and periodic driving, we perform these numerical calculations for the following set of parameters, $E_g=0.45$ eV, $E_r=0.15$ eV, $V=5\times10^{-4}$ eV, and $T=300$ K. This chosen set of parameters is typical for the ET in some types of metalloproteins [35]. The quantities Δ, ν, Ω, and $\zeta=d\mathcal{E}_0/\hbar\Omega$ have been varied independently from one to another. Figures 1 and 2 show the ET rate in dependence on the amplitude of the regular field with frequency $\hbar\Omega=1$ eV, and in dependence on the amplitude of the dichotomic fluctuations at two different frequencies.

Let us start the discussion with an analysis of the influence of dichotomic fluctuations in the absence of the periodic field ($\zeta=0$). A comparison between Figs. 1(a) and 2(a) shows that the dependence of the effective transfer rate on the amplitude of the fluctuations is quite different for the case of fast fluctuations with $\nu=10^{12}$ s^{-1}, and for the case with $\nu=10^6$ s^{-1}. In the first case, the rate increases exponentially with Δ, and has two maxima which approximately correspond to the maxima of the forward and backward rates. On the whole, the transfer process is single exponential with a small parameter $\chi<10^{-3}$. (The dependence of χ on ζ and Δ is not shown in this case, since it is of less interest.) In the second case of the transfer is mainly nonexponential (see Fig. 3 for the behavior of χ). Additionally, the dependence of Γ on Δ is quite different. Γ decreases and reaches at $\hbar\Delta>0.1$ eV the constant value $\Gamma\sim10^6$ s^{-1}, which indicates that the transfer proceeds in the gated regime. For fast as well as slow fluctuations, the variation of the effective energy gap $\varepsilon_{\mathrm{eff}}$ with Δ demonstrates that externally applied noise may invert the transfer direction. We would like to stress this very important result, which indicates that the direction of the ET can proceed again the averaged energy bias due to strongly correlated fluctuations. The explanation for this unusual behavior, however, is quite simple if one accepts the adiabatic approximation introduced by Eqs. (13) and (14).

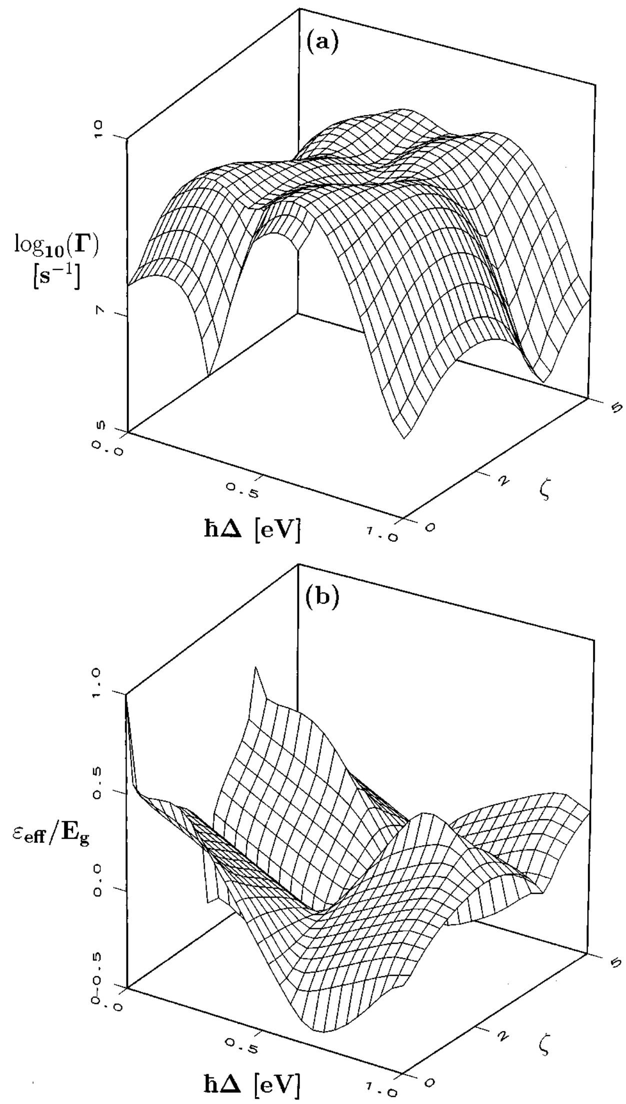

FIG. 1. Effective transfer rates Γ (curve *a*) and effective energy gap $\varepsilon_{\mathrm{eff}}$ (curve *b*) vs the noise amplitude Δ and the coupling strength ζ for a jump frequency $\nu=10^{12}$ s^{-1}. Other parameters are given in the text.

In the considered case this approximation results in the rate expression

$$k^{\pm}=\frac{2\pi}{\hbar}\frac{V^2}{\sqrt{4\pi E_rk_BT}}\{e^{-(E_g^{\pm}-E_r)^2/4E_rk_BT}+e^{-(E_g^{\pm}+E_r)^2/4E_rk_BT}\}, \tag{16}$$

which is the sum of the forward and backward rates well known in the Marcus theory of ET reactions in condensed media [36]. Without periodic driving, this approximation is quite applicable for the discussed range of parameters. It

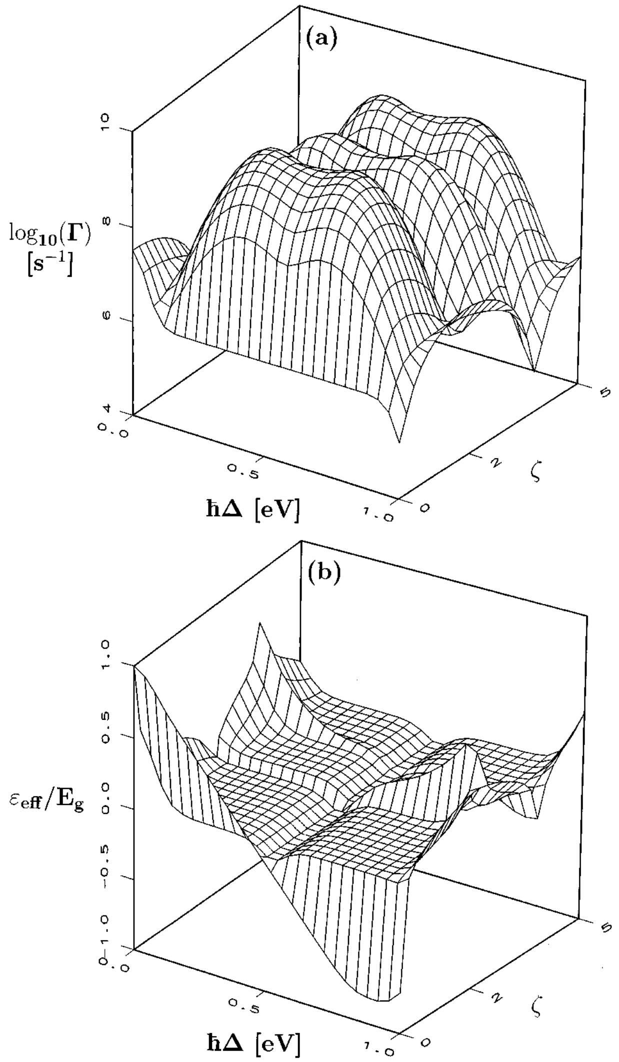

FIG. 2. Effective transfer rates Γ (curve a) and effective energy gap $\varepsilon_{\rm eff}$ (curve b) vs the noise amplitude Δ and the coupling strength ζ for a jump frequency $\nu = 10^6 \ {\rm s}^{-1}$. Other parameters are given in the text.

states that the nonadiabatic ET rate follows *adiabatically* the actual position of the free-energy gap $E_g(t)$ which jumps between two values $E_g^+ > 0$ and $E_g^- < 0$. The positive energy value corresponds to the direct transfer, and the negative one is related to the inverted transfer. The probabilities of the conformational states corresponding to $E_g^+ > 0$ and $E_g^- < 0$ are identical. But the *nonmonotonic* dependence of $k_0^\pm$ on $E_g^\pm$, Eq. (16), leads to the result that the rate of the inverted transfer k_0^- is larger than the rate k_0^+ of the direct transfer. For this reason, the averaged transfer takes place in the inverted direction despite the fact that the averaged energy gap is positive. Using this effect, one would be able to construct a molecular device (at least in principle) which could extract useful work from strongly correlated *nonequilibrium* fluctuations. A number of similar results have been recently reported in the field of classical physics [24]. In relation to this conclusion we have to stress here how dangerous it could be to model an environment staying in thermal *equilibrium* by a strongly correlated *external* noise [23].

Furthermore, in comparison of parts (a) and (b) of Fig. 2, we may conclude that such a gated regime exists in which the transfer direction can be inverted, although the transfer rate itself is not affected. Figures 4(a) and 4(b) demonstrate the dependence of the effective rate and the effective energy gap on the frequency of the fluctuations at fixed amplitude $\hbar\Delta = 0.15$ eV. Here the free-energy gap jumps between $E_g^+ = 0.6$ eV and $E_g^- = 0.3$ eV. It can be also deduced from Fig. 4(a) that the ET changes from the nonadiabatic type of transfer at $\nu < 10^4 \ {\rm s}^{-1}$ to the gated transfer at $10^4 \ {\rm s}^{-1} < \nu < 10^9 \ {\rm s}^{-1}$, and then again back to the nonadiabatic type what is in accordance with the criterion of Eq. (15).

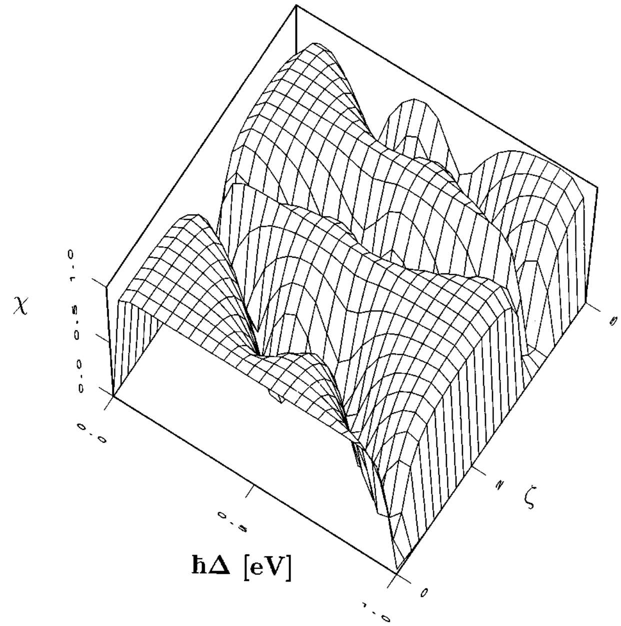

FIG. 3. χ vs the noise amplitude Δ and the coupling strength ζ for a jump frequency $\nu = 10^6 \ {\rm s}^{-1}$. Other parameters are given in the text.

To discuss the influence of the periodic driving, we neglect the dichotomic fluctuations $(\Delta = 0)$ in a first step. Under such circumstance the periodic field can suppress the ET [Figs. 1 and 2(a)], it can enhance it (not shown), but it can also invert the direction of the transfer [Figs. 1 and 2(a)]. This behavior has been already discussed in Refs. [7,12], and we will concentrate in the following on the additional effects introduced by a dynamically disordered free-energy gap. The most interesting ET regime might be the periodic field-induced crossover from the gated to the nonadiabatic ET [Figs. 2(a) and 4(a)]. If this crossover appears, the ET could change from nonexponential to single-exponential behavior (Fig. 3). An additional effect of interest occurs at moderate amplitudes of the fluctuation, i.e., at $0.15 \ {\rm eV} < \hbar\Delta < 0.5$ eV, and at large frequencies (Fig. 1). One can conclude from Fig. 1 that a regime is possible in which the transfer is nonadiabatic, and its rate is only slightly affected by periodic field, but the direction of transfer can be inverted. Such a behavior may appear if the transfer is almost activationless due to the combined action of the quantum dissipation and the dichotomic fluctuations. To realize such an effect the field strength $\mathcal{E}_0$ has to be of the order of 10^6–10^7 V/cm at a transfer distance of $r > 10$ Å [7,12].

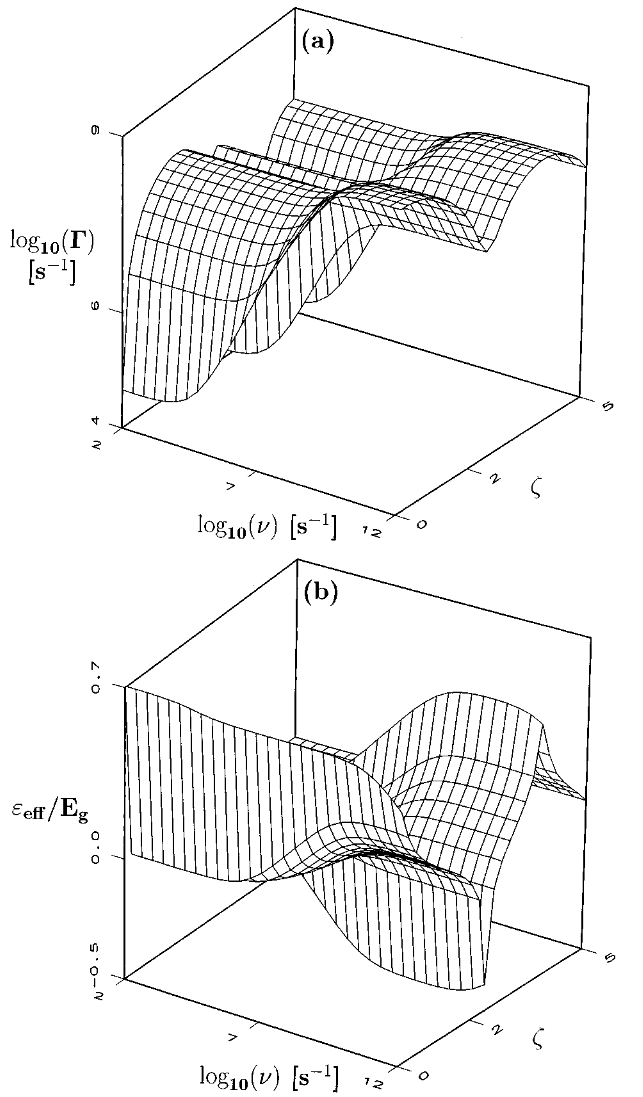

FIG. 4. Effective transfer rates Γ (curve a) and effective energy gap $\varepsilon_{\rm eff}$ (curve b) vs the noise frequency ν and the coupling strength ζ for a noise amplitude $\hbar\Delta = 0.15$ eV. Other parameters are given in the text.

Note also that, in the absence of the periodic field, the effect of transfer inversion by dichotomic fluctuations becomes stronger at low jump frequencies [Figs. 1(b) and 2(b)]. At low jump frequencies, however, the periodic field tends to smear out this effect completely [Figs. 2(b) and 4(b)].

V. CONCLUSIONS

In the present paper, a generalization of the standard spin-boson model which results from the inclusion of a time-dependent energy bias has been studied. It has been provided that this time dependence originates from two different sources. One was assumed to be a random process modeled as a dichotomic Markov process. The other source was treated as statistically independent, but quite arbitrary in others aspects. Starting from the generalized master equation for the driven spin-boson model, Eq. (2), which was obtained earlier in NIBA [3,5,6,11] we initially arrived at the exact averaging of this equation with respect to the dichotomic fluctuations. The resulting set of integrodifferential equations (5) generalizes our previous result [see Eq. (27) in Ref. [11]] to the case of an additional time dependence of the energy bias. They can be used in a number of forthcoming applications, including either regular or stochastic driving fields. Here the approach was applied to the case of single harmonic external field. The averaged transient dynamics for this model was considered in the limit of a fast nonadiabatic driving and in the Markov approximation. Within this approximation an expression for the effective transient rate (12) could be obtained with coefficients given by expansion (8) and Eq. (9). This expression allows us to trace the influence of the dichotomic and periodic driving. For the case of a strongly asymmetric TLS, one can predict the gating of the transfer achieved by dichotomic noise. Additionally, the switching between different transfer regimes by applying a strong periodic field could be proposed.

To illustrate the main ideas of this work, we choose the model of the periodically driven long-range ET in a protein, which additionally undergoes nonequilibrium fluctuations between two conformations. The influence of low-frequency protein vibrations on the transfer process was taken into account in the quasiclassical approximation and in the high-temperature limit. It was possible to demonstrate the inversion of the transfer direction against the mean energy bias merely by dichotomic fluctuations when the periodic field is absent. It is interesting to note that such an inversion could happen despite the fact that the effective transfer rate is not affected (gated regime).

This noise-induced inversion of the transfer direction bears some resemblance to similar effects of *nonequilibrium* noises found recently for classical diffusional systems [24]. In the related domain, the possibility of noise-induced directional diffusion in unbiased systems has been discovered. In our case, however, we have a somewhat different situation, when the already existing energetic bias can effectively be inverted by correlated fluctuations.

Furthermore, it was shown that the periodic field can destroy the gated regime, and can essentially enhance the rate of transfer. Its influence depends on the rate and amplitude of the fluctuations. For example, it can invert the transfer direction in the case of fast fluctuations, but does not cause this effect at slow ones.

ACKNOWLEDGMENTS

Financial support for this work by the *Volkswagen-Stiftung*, Germany, is gratefully acknowledged.

[1] M. Grifoni, M. Sassetti, J. Stockburger, and U. Weiss, Phys. Rev. E **48**, 3497 (1993).
[2] M. Grifoni, M. Sassetti, P. Hänggi, and U. Weiss, Phys. Rev. E **52**, 3596 (1995).
[3] M. Grifoni, M. Sassetti, and U. Weiss, Phys. Rev. E **53**, R2033 (1996); M. Grifoni, *ibid.* **54**, R3086 (1996).
[4] T. Dittrich, B. Oeschlagel, and P. Hänggi, Europhys. Lett. **22**, 5 (1993); Acta Phys. Pol. B **94**, 845 (1993).
[5] Yu. Dakhnovski, Ann. Phys. (N.Y.) **230**, 145 (1994).
[6] Yu. Dakhnovskii, Phys. Rev. B **49**, 4649 (1994).
[7] Yu. Dakhnovskii and R. D. Coalson, J. Chem. Phys. **103**, 2908 (1995); Yu. Dakhnovskii, D. G. Evans, H. J. Kim, and R. D. Coalson, *ibid.* **103**, 5459 (1995).
[8] E. G. Petrov, Teor. Mat. Fiz. **68**, 117 (1986) (in Russian); E. G. Petrov and V. I. Teslenko, Theor. Math. Phys. **84**, 986 (1990); E. G. Petrov, V. I. Teslenko, and I. A. Goychuk, Phys. Rev. E **49**, 3894 (1994).
[9] V. G. Bar'yakhtar and E. G. Petrov, *Kinetic Phenomena in Solids* (Naukova Dumka, Kiev, 1989) (in Russian).
[10] I. A. Goychuk, E. G. Petrov, and V. May, Phys. Rev. E **51**, 2982 (1995); J. Chem. Phys. **103**, 4937 (1995).
[11] I. A. Goychuk, E. G. Petrov, and V. May, Phys. Rev. E **52**, 2392 (1995).
[12] I. A. Goychuk, E. G. Petrov, and V. May, Chem. Phys. Lett. **253**, 428 (1996).
[13] E. G. Petrov, I. A. Goychuk, and V. May, Physica A **233**, 560 (1996); Phys. Rev. E **54**, 4726 (1996).
[14] D. E. Makarov and N. Makri, Phys. Rev. E **52**, 5863 (1995).
[15] M. Morillo and R. I. Cukier, Phys. Rev. B **54**, 13 962 (1996).
[16] A. J. Leggett, S. Chakravarty, A. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[17] U. Weiss, *Quantum Dissipative Systems*, Series in Modern Condensed Matter Physics Vol. 2 (World Scientific, Singapore, 1993).
[18] K. Lindenberg and B. J. West, *The Nonequilibrium Statistical Mechanics of Open and Closed Systems* (VCH, New York, 1990).
[19] A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985); J. N. Onuchic, D. N. Beratan, and J. J. Hopfield, J. Phys. Chem. **90**, 3707 (1986).
[20] M. Grifoni and P. Hänggi, Phys. Rev. E **54**, 1390 (1996).
[21] E. G. Petrov, I. A. Goychuk, and V. May, Phys. Rev. E **54**, R4500 (1996); I. A. Goychuk, E. G. Petrov, and V. May, J. Chem. Phys. **106**, 4522 (1997).
[22] T. Y. Tsong and R. D. Astumian, Prog. Biophys. Mol. Biol. **50**, 1 (1987); R. D. Astumian, P. B. Chock, T. Y. Tsong, and H. V. Westerhoff, Phys. Rev. A **39**, 6416 (1989).
[23] The modeling of the dissipative influence of an environment by external noise is one of the commonly used approaches known generally as the Langevin approach in classical physics [28] or as the stochastic Liouville equation approach in quantum physics [27,18]. Though this method is generally applicable, sometimes it should be used with some care to model an equilibrium environments [28,18]. Otherwise, paradoxes connected with the violation of the second law of thermodynamics, like Brillouin's paradox [28], could appear. Note, however, that this approach seems to be quite reliable to model the nonequilibrium parts of the environment [13].
[24] M. O. Magnasco, Phys. Rev. Lett. **71**, 1477 (1993); R. D. Astumian and M. Bier, *ibid.* **72**, 1466 (1994); R. Bartussek, P. Hänggi, and J. G. Kissner, Europhys. Lett. **28**, 459 (1994).
[25] *Long-Range Electron Transfer in Biology*, edited by G. Palmer (Springer, Berlin, 1991).
[26] M. Bixon, J. Jortner, M. E. Michel-Beyerle, and A. Ogrodnik, Biochim. Biophys. Acta **977**, 273 (1989).
[27] V. M. Kenkre and P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates* (Springer-Verlag, Berlin, 1982).
[28] N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry, 2-d, Enlarged and Extended Edition* (North-Holland, Amsterdam, 1992).
[29] R. C. Bourret, U. Frisch, and A. Pouquet, Physica (Amsterdam) **65**, 303 (1973).
[30] I. A. Goychuk, Phys. Rev. E **51**, 6267 (1995).
[31] V. E. Shapiro and V. M. Loginov, Physica A **91**, 563 (1978).
[32] R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic System*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962).
[33] In order to determine MRT uniquely, one has yet to remove the artificial dependence of the averaged transient dynamics on the initial value of the correlator $\overline{\langle \alpha(t)\sigma_z(t)\rangle}$. This can be achieved by an additional averaging or by choosing the steady-state value of this correlator as initial.
[34] J. N. Gehlen, M. Marchi, and D. Chandler, Science **263**, 499 (1994).
[35] J. N. Onuchic, J. Chem. Phys. **86**, 3925 (1987); R. F. Goldstein and A. Bearden, Proc. Natl. Acad. Sci. USA **81**, 135 (1984).
[36] R. A. Marcus, J. Chem. Phys. **24**, 966 (1956); **24**, 979 (1956); V. G. Levich and R. R. Dogonadze, Dokl. Akad. Nauk **124**, 123 (1959) [Proc. Acad. Sci. Phys. Chem. Sect. **124**, 9 (1959)].