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Stochastically averaged master equation for a quantum-dynamic system interacting with a thermal bath

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The methods of nonequilibrium density-matrix and coarse-temporal conception are used to obtain the kinetic equation for the parameters $\gamma_{nm}(t) = \mathrm{Sp}[\hat{\rho}(t)|n\rangle\langle m|]$ of a quantum dynamic system (QDS) interacting with a thermal bath and external stochastic field. It is important that the stochastic field is taken exactly into consideration. For diagonal QDS parameters $\gamma_{nn}(t)$ this equation is reduced to the generalized Pauli equation (GPE) with stochastic time-dependent coefficients $w_{nm}(t)$. Special attention is given to the procedure of averaging over stochastic processes. It is shown that after averaging over energy fluctuations affected by the stochastic field, in the first cumulant approximation in terms of stochastic processes $w_{nm}(t)$, the GPE is transformed to the Pauli equation for the QDS state population $P_n(t) = \langle\gamma_{nn}(t)\rangle_f$. As an example, the relaxation behavior of a two-level system interacting with a dichotomous field (dichotomous Markovian process of kangaroo type) and a harmonic oscillator coupled with a thermal bath is considered. It is shown that the probability of relaxation transitions between energy levels may be changed by several orders of magnitude under the influence of the dichotomous field.

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I. INTRODUCTION

There is a great number of physical systems where a few relevant quantum variables are strongly separated from the other ones. These quantum variables can be treated as the quantum-dynamical system (QDS) that interacts weakly with remaining variables called the thermal bath. The bath is considered as a quantum statistical system being at equilibrium. Therefore, QDS relaxes from its initial nonequilibrium state to the equilibrium one due to the influence of QDS–thermal-bath interaction. This interaction connects the energetic transitions in QDS with those in thermal bath. The nature of thermal bath and QDS-bath interaction depends essentially on the real physical media (crystals, liquids, macromolecular structures, plasma, gas) and real transitional processes (for example, energy and charge transfer). Nevertheless, despite its different physical nature, any thermal bath has very important common property. Namely, each bath contains the infinite number of degrees of freedom and, hence, the continuous or quasicontinuous energy spectrum. As a result the final irreversibility of quantum relaxation transitions in QDS is directly connected with transitions in the continuous spectrum of thermal bath (see, for example, [1]).

There is a based universal method used to describe relaxation processes in QDS being in contact with thermal bath. This method is based on the introduction of the density matrix for the whole (QDS and bath) system. Using the Liouville equation and the projection operator technique to eliminate thermal-bath variables, Nakajima [2] and Zwanzig [3] obtained the closed reduced equation for the diagonal part of this density matrix. Nakajima-Zwanzig approach was used by many other authors (see, for instance, [4,5]) to obtain for QDS the generalized master equation (GME), that is reduced in the Markovian limit to the Pauli balance equation [6]

$$\frac{\partial P_n(t)}{\partial t} = \sum_{m\neq n}[w_{mn}P_m(t) - w_{nm}P_n(t)] \tag{1.1}$$

for the population $P_n(t)$ of the nth QDS state. These populations satisfy the normalization condition

$$\sum_n P_n(t) = 1. \tag{1.2}$$

Equation (1.1) is valid on the time scale $t > \tau_0$ where τ_0 is the correlation time for memory function [4]. At $t > \tau_0$ the memory function does not depend on time t and coincides with time-independent value w_{nm} in (1.1). The latter characterizes the probability per time unit to make a transition in QDS from the state $|n\rangle$ to the state $|m\rangle$ $(n \neq m)$. The real calculation of w_{nm} is connected with perturbation theory and, consequently, with the choosing of the QDS Hamiltonian H_0, thermal-bath Hamiltonian H_T, and the QDS-bath interaction V. In the simplest cases one may use the "golden rule" to calculate the time-independent transition probability w_{nm}. In more complicated cases the situation is not so simple [7] and the master equation in the Pauli equation form is, generally invalid.

To avoid such kind of difficulties one may use the stochastic theory approach to the description of relaxation. This theory is based on stochastic Liouville equation introduced by Kubo [8] and have been developed by different authors in numerous studies [9–16]. The main idea of this approach is to treat the QDS-bath coupling

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phenomenologically and semiclassically via the introduction of a stochastic term in the QDS Hamiltonian. This approach is not, however, free from difficulties. The main problem is that the stochastic influence taken alone does not lead to thermal equilibrium in QDS [14,17]. This difficulty has been phenomenologically solved by the introduction of the relaxation term in the QDS Liouville equation [18,19]. Because of the strong influence of external field on the relaxation constants [20,21] this phenomenological method is however not quite correct.

Rather successful efforts to solve correctly the problems mentioned above have been made by Fox [14,17] and, more recently, by Villaeys, Boeglin, and Lin [22]. The kinetic equation was obtained in the case of stochastic influence modeled by white or weakly colored Gaussian Markovian noise. But in the real system such idealization is not always valid. This circumstance requires a development of the appropriate method to obtain the kinetic equations for relaxation processes in the case when both the quantum-thermal bath and strong colored noise are simultaneously taken into account.

The aim of the present work is to obtain the master equation in the case when the stochastic field is taken exactly into consideration and the QDS-bath interaction is treated as weak perturbation. Below, under thermal bath one means the medium where the equilibrium time τ_{eq} is short enough to use the course-temporal conception. In accordance with such a conception, relaxation transitions in QDS are realized on a background of more fast energy fluctuations occurring in bath. The coarse-temporal conception has been first introduced by Von Neuman [23] for the macroscopic quantum system. Then Bogolyubov [24] and more recently Peletminskii [25,26] using both the Von Neuman concept and the principle of weakening of correlations have formulated the ergodic relations for the coarse-temporal density matrix $\rho^{\text{ct}}[\gamma_{nm}(t)]$. This matrix depends on time through time dependence of the QDS parameters $\gamma_{nm}(t)$. For quantum systems, the parameters $\gamma_{nm}(t)$ correspond to the Hubbard operators $\hat{\gamma}_{nm} = | n\rangle\langle m |$ whose set is considered to be complete. Therefore, the problem is to derive the kinetic equation for the parameters $\gamma_{nm}(t)$ and then, by making an average over energy fluctuations, to obtain the Pauli equations for the state populations

$$P_n(t) = \langle \gamma_{nn}(t) \rangle_f . \tag{1.3}$$

Here, the subscript f shows the average over energy fluctuations.

The method of a kinetic equation for parameters $\gamma_{nm}(t)$ of the quantum systems was developed in many studies (see, in detail, [27]). In this paper we use the Akhiezer-Peletminskii method (the so-called nonequilibrium density-matrix method [26]) to investigate the problem of stochastization of quantum energy levels. According to [28] it is possible to substitute the mathematically idealized discrete stochastic process with known average characteristics for the real fluctuations of the quantum system parameters. After such a substitution we consider this stochastic process as an external quasiclassical stochastic field in terms of the Akhiezer-Peletminskii approach for a quantum system interacting with thermal bath and strong external fields [27,20,21]. The great advantage of such an approach is that the stochastic field may be arbitrarily strong. The only restriction is a requirement for the stochastic field parameters to be independent on the dynamic variables of QDS and thermal bath.

In this paper we formulate the principle of weakening of correlations for the case of external stochastic field (Sec. II) and obtain the non-Markovian kinetic equations for the QDS parameters $\gamma_{nm}(t)$ (Sec. III). It is also shown that in some simple cases the relaxation dynamics of quantum systems may be described by the stochastic master equation similar to (1.1), that is by generalized Pauli equation, GPE. Further, we discuss the problem of stochastic averaging of these equations, especially in the case of fast stochastization (Sec. IV). Finally, we show the possibilities of the general theory by investigation of the relaxation behavior of two-level system interacting with the dichotomous field (Sec. V).

II. WEAKENING CORRELATION PRINCIPLE AND INTEGRAL EQUATION

In this section we reduce the Liouville equation to the integral equation for the coarse-temporal density matrix of the whole QDS–thermal-bath system.

A. Model Hamiltonian

We consider the whole system as the sum of the thermal bath and QDS being under the influence of the external stochastic field. Let us assume that in spite of the stochastic field action, the whole system Hamiltonian can be divided into time-dependent and time-independent terms,

$$H(t) = H_0(t) + V(t) + H_T , \tag{2.1}$$

where $H_0(t)$ is the QDS Hamiltonian, $V(t)$ is the operator of weak interaction between QDS and thermal bath, and

$$H_T = \sum_{\lambda} \Omega_\lambda (\hat{B}_\lambda^+ \hat{B}_\lambda + \tfrac{1}{2}) \tag{2.2}$$

is the Hamiltonian of the thermal bath. Ω_λ is the frequency of the λth bath mode, $\hat{B}_\lambda^\dagger$ ($\hat{B}_\lambda$) is the creation (annihilation) operator (here and further on we use the system of units in which the Plank constant $\hbar = 1$).

Due to the completeness of a set of the Hubbard operators $\hat{\gamma}_{nm} = | n\rangle\langle m |$, the operators $H_0(t)$ and $V(t)$ can be expanded over $\hat{\gamma}_{nm}$ as [21]

$$H_0(t) = \sum_{nm} H_{nm}(t) \hat{\gamma}_{nm}, \tag{2.3}$$

$$V(t) = \sum_{nm} \hat{F}_{nm}(t) \hat{\gamma}_{nm} . \tag{2.4}$$

The corresponding expression for the QDS density matrix $\rho(t) \equiv \rho(\gamma(t))$ is given by

$$\rho(t) = \sum_{nm} \gamma_{nm}(t)\hat{\gamma}^{\dagger}_{nm}. \tag{2.5}$$

The coefficients $H_{nm}(t)$ and $\gamma_{nm}(t)$ of the expansions (2.3) and (2.5) are the parameters of a quantum system. The operators of expansion (2.4), $\hat{F}_{nm}(t)$, depend on the bath variables. The expansions (2.3)–(2.5) are quite general ones. They will be used to obtain the general kinetic equations for parameters $\gamma_{nm}(t)$ in Secs. II C and III A.

As an example, in the simplest case the coefficients $H_{nm}(t)$ and operators $\hat{F}_{nm}(t)$ may be expressed in the form

$$H_{nm}(t) = [\omega_n + \varepsilon_n(t)]\delta_{nm}, \tag{2.6}$$

$$\hat{F}_{nm}(t) = \hat{F}_{nm} = \frac{1}{2}\sum_{pl,p\neq l}\sum_{\lambda}\kappa^{\lambda}_{pl}(\delta_{np}\delta_{ml} + \delta_{nl}\delta_{mp}) \times(\hat{B}^{\dagger}_{\lambda} + \hat{B}_{\lambda}) \ , \tag{2.7}$$

where ω_n is the spectrum of nonperturbated quantum system, $\varepsilon_n(t)$ is the energy addition to ω_n due to the stochastic field, and $\kappa^{\lambda}_{nm} = (\kappa^{\lambda}_{mn})^*$ are the relaxation parameters. In this case the stochastic field influences only the diagonal parameters of the quantum system, and the expressions (2.3) and (2.4) are written as

$$H_0(t) = \sum_{n}[\omega_n + \varepsilon_n(t)] \mid n\rangle\langle n \mid, \tag{2.8}$$

$$V(t) = V = \frac{1}{2}\sum_{nm,n\neq m}\kappa^{\lambda}_{nm}(\mid n\rangle\langle m \mid + \mid m\rangle\langle n \mid) \times(\hat{B}^{\dagger}_{\lambda} + \hat{B}_{\lambda}). \tag{2.9}$$

The form (2.7) of the operator $\hat{F}_{nm}$ and, therefore, the interaction (2.9) corresponds to the approximation where transitions in the QDS are accompanied by creation or annihilation of a single phonon in the thermal bath. These expressions will be used in Sec. III B to obtain the closed equations for the parameters $\gamma_{nn}(t)$, i.e., the generalized master equation.

B. Liouville equation

According to the Bogolyubov's functional hypothesis, the density matrix ρ_{ST} of the whole system (QDS and thermal bath) reduces on the time scale $t \gg \tau_{\text{eq}}$ to the coarse-temporal density-matrix

$$\rho_{ST}(t) \longrightarrow \rho^{\text{ct}}(\gamma(t)) \ , \tag{2.10}$$

where τ_{eq} is the above mentioned equilibrium time in the thermal bath. Let us write the Liouville equation for the coarse-temporal density matrix of a system

$$\frac{\partial\rho^{\text{ct}}(t)}{\partial t} = i[\rho^{\text{ct}}(t), H_0(t) + V(t) + H_T]. \tag{2.11}$$

The formal solution of (2.11) is given by

$$\rho^{\text{ct}}(t) = \mathcal{U}(t)\rho^{\text{ct}}(0)\mathcal{U}^{\dagger}(t) + i\int_{-t}^{0} d\tau\,\mathcal{U}^{\dagger}(t+\tau;t) \times[\rho^{\text{ct}}(t+\tau), V(t+\tau)]\mathcal{U}(t+\tau;t). \tag{2.12}$$

Here we introduce the single- and double-time evolution operators determined by the relations

$$\frac{\partial\mathcal{U}(t)}{\partial t} = -i(H_0(t) + H_T)\mathcal{U}(t),$$

$$\mathcal{U}(0) = \mathcal{U}^{\dagger}(0) = 1, \mathcal{U}^{\dagger}(t) = \mathcal{U}^{-1}(t),$$

$$\mathcal{U}^{\dagger}(t)\mathcal{U}(t) = \mathcal{U}(t)\mathcal{U}^{\dagger}(t) = 1,$$

$$\mathcal{U}(t+\tau;t) = \mathcal{U}(t+\tau)\mathcal{U}^{\dagger}(t),$$

and then formally

$$\mathcal{U}(t) = \exp(-iH_T t)\hat{T}\exp\left(-i\int_0^t H_0(t')dt'\right),$$
$$\mathcal{U}(t+\tau;t) = \exp(-iH_T\tau)\hat{T}\exp\left(-i\int_t^{t+\tau} H_0(t')dt'\right) , \tag{2.13}$$

where $\hat{T}$ is the Dayson chronological operator. Equation (2.12) is an exact one at least with an accuracy to the coarse-temporal condition (2.10). Hereafter, we will find the approximate solution of Eq. (2.12) by using the expansion of the density matrix $\rho^{\text{ct}}(t)$ over the interaction V in the form

$$\rho^{\text{ct}}(t) = \rho^{\text{ct}}_0(t) + \rho^{\text{ct}}_1(t) + \cdots \ , \tag{2.14}$$

where at $V \to 0$ the first order term $\rho_1^{(\text{ct})}(t) \to 0$. This solution must comply with the following asymptotic boundary condition:

$$\lim_{t\to-\infty}\{\mathcal{U}^{\dagger}(t)[\rho^{\text{ct}}(t) - \rho(t)\rho_T]\mathcal{U}(t)\} = 0 \tag{2.15}$$

[due to the supposition that at $t \to -\infty$ the interaction is absent, $V(t) = 0$]. The relation (2.15) that expresses the principle of the weakening of correlations will be used in the next subsection to obtain the service integral equation. In Eq. (2.15) $\rho(t)$ and ρ_T are the density matrices of the QDS and thermal bath, respectively. The density matrix of the thermal bath,

$$\rho_T = \exp(-H_T/k_BT)[\text{Tr}\exp(-H_T/k_BT)]^{-1}, \tag{2.16}$$

is supposed to be equilibrium. In (2.16) k_B is the Boltzmann constant, T is the absolute temperature, and the symbol Tr denotes the trace over the bath states.

C. Integral equation

In this subsection we obtain the integral equation which is asymptotically equivalent to the exact Eq. (2.12). Let us introduce the double-time values in the form

$$\begin{aligned} \rho^{\mathrm{ct}}(t;\tau) &= \mathcal{U}(t+\tau;t)\rho^{\mathrm{ct}}(t)\mathcal{U}^{\dagger}(t+\tau;t), \\ \hat{\gamma}_{nm}(t;\tau) &= \mathcal{U}^{\dagger}(t+\tau;t)\hat{\gamma}_{nm}\mathcal{U}(t+\tau;t), \\ \gamma_{nm}(t;\tau) &= \mathrm{Sp}[\rho^{\mathrm{ct}}(t;\tau)\hat{\gamma}_{nm}]\ , \end{aligned} \qquad (2.17)$$

where Sp denotes the trace operation over the states of the whole system. At $V = 0$ the expressions (2.13)–(2.17) yield

$$\begin{aligned} \rho_0^{\mathrm{ct}}(t;\tau) &= \rho(\gamma(t;\tau))\rho_T \\ &= \mathcal{U}(t+\tau;t)\rho(t)\rho_T\mathcal{U}^{\dagger}(t+\tau;t)\ . \end{aligned} \qquad (2.18)$$

Let us differentiate the relation (2.18) over τ. Then combining the result of differentiation with the relations (2.17), Eq. (2.11) and the equation

$$\frac{\partial\rho(t+\tau)}{\partial\tau} = \sum_{nm}\frac{\partial\rho(t+\tau)}{\partial\gamma_{nm}(t+\tau)}\frac{\partial\gamma_{nm}(t+\tau)}{\partial\tau}$$

we obtain

$$\begin{aligned} &\mathcal{U}(t+\tau;t)[H_0(t+\tau)+H_T,\rho(t)\rho_T]\mathcal{U}^{\dagger}(t+\tau;t) \\ &\qquad = i\sum_{nm}\frac{\partial\rho(t;\tau)\rho_T}{\partial\gamma_{nm}(t;\tau)}\frac{\partial\gamma_{nm}(t;\tau)}{\partial\tau}. \end{aligned} \qquad (2.19)$$

By using the relations (2.14)–(2.19) in Eq. (2.12), we can write

$$\begin{aligned} \rho^{\mathrm{ct}}(t) - \rho(t)\rho_T = \mathcal{U}(t)[\rho^{\mathrm{ct}}(t) - \rho(t)\rho_T]\mathcal{U}^{\dagger}(t) - i\int_{-t}^{0} d\tau\,\mathcal{U}^{\dagger}(t+\tau;t)\Bigg[&[V(t+\tau),\rho^{\mathrm{ct}}(t+\tau)] \\ -i\sum_{nm}\frac{\partial\rho(t+\tau)\rho_T}{\partial\gamma_{nm}(t+\tau)}\left(\frac{\partial}{\partial t}\gamma_{nm}(t+\tau) - L_{nm}^{(0)}(t+\tau)\right)\Bigg]&\mathcal{U}(t+\tau;t)\ , \end{aligned} \qquad (2.20)$$

where

$$\begin{aligned} L_{nm}^{(0)}(t) &= i\mathrm{Sp}\{\rho(t)\rho_T[H_0(t)+H_T,\hat{\gamma}_{nm}(t,0)]\}, \\ \sum_{nm}\frac{\partial\rho(t)\rho_T}{\partial\gamma_{nm}(t)}L_{nm}^{(0)}(t) &= -i[H_0(t)+H_T,\rho(t)\rho_T]. \end{aligned} \qquad (2.21)$$

Finally, by combining (2.21) with Eqs. (2.15) and (2.20) we can easily find the difference $\rho^{\mathrm{ct}}(0) - \rho(0)\rho_T$ and, after all, obtain the integral equation in the form

$$\begin{aligned} \rho^{\mathrm{ct}}(t) = \rho(t)\rho_T - i\int_{-\infty}^{0} d\tau\,\mathcal{U}^{\dagger}(t+\tau;t)\Bigg[&[V(t+\tau),\rho^{\mathrm{ct}}(t+\tau)] \\ -i\sum_{nm}\frac{\partial\rho(t+\tau)\rho_T}{\partial\gamma_{nm}(t+\tau)}\left(\frac{\partial}{\partial t}\gamma_{nm}(t+\tau) - L_{nm}^{(0)}(t+\tau)\right)\Bigg]&\mathcal{U}(t+\tau;t). \end{aligned} \qquad (2.22)$$

This integral equation is used in the next section to calculate the second order term in the kinetic equations.

III. KINETIC EQUATIONS

Here we derive the kinetic equations for the QDS parameters $\gamma_{nm}(t)$ and then obtain the reduced kinetic equations for the QDS populations $\gamma_{nn}(t)$.

A. General kinetic equations

According to the Akhiezer-Peletminskii density-matrix method [26] the kinetic equations for the parameters $\gamma_{nm}(t)$ of the quantum system are given by

$$\begin{aligned} \frac{\partial}{\partial t}\gamma_{nm}(t) &= i\mathrm{Sp}(\rho^{\mathrm{ct}}(t)[H_0(t)+H_T+V(t),\hat{\gamma}_{nm}]) \\ &= L_{nm}^{(0)}(t) + L_{nm}^{(1)}(t) + L_{nm}^{(2)}(t) + \cdots\ , \end{aligned} \qquad (3.1)$$

where the zero, first, and second order terms of the expansion of $L_{nm}(t)$ over the interaction $V(t)$ are defined by the expressions

$$L_{nm}^{(0)}(t) = i\mathrm{Sp}(\rho^{\mathrm{ct}}(t)[H_0(t)+H_T,\hat{\gamma}_{n}m])\ ,$$

$$L_{nm}^{(1)}(t) = i\mathrm{Sp}(\rho_0^{\mathrm{ct}}(t)[V(t),\hat{\gamma}_{nm}]), \qquad (3.2)$$

$$L_{nm}^{(2)}(t) = i\mathrm{Sp}(\rho_1^{\mathrm{ct}}(t)[V(t),\hat{\gamma}_{nm}]),$$

respectively. The Eqs. (3.1) and (3.2) have been first obtained by Peletminskii and Yatsenko [25] for the case of the time-independent external field. Then these equations were reproduced by several authors for a more general case (for references see [27,21,20]). In presence of the stochastic field Eqs. (3.1) and (3.2) remain formally the same.

Let us consider the expression

$$\begin{aligned} \rho_1^{\mathrm{ct}}(t) = -i\int_{-\infty}^{0} d\tau\,\mathcal{U}^{\dagger}(t+\tau;t)\Bigg(&[V(t+\tau),\rho(t+\tau)\rho_T] \\ -i\sum_{nm}\frac{\partial\rho(t+\tau)\rho_T}{\partial\gamma_{nm}(t+\tau)}L_{nm}^{(1)}(t+\tau)\Bigg)&\mathcal{U}(t+\tau;t) \end{aligned} \qquad (3.3)$$

which follows from Eq. (2.22). Using the relations

$$\hat{\gamma}_{nn'}\hat{\gamma}_{mm'} = \delta_{mn'}\hat{\gamma}_{nm'},$$

$$\mathrm{Sp}(\hat{\gamma}_{nn'}\hat{\gamma}_{mm'}) = \delta_{mn'}\delta_{nm'}\ ,$$

for the Hubbard operators and expansion of the commutator $[V(t),\hat{\gamma}_{nm}]$ over the Hubbard operators we obtain

$$\sum_{nm}\frac{\partial\rho(t+\tau)\rho_T}{\partial\gamma_{nm}(t+\tau)}L^{(1)}_{nm}(t) = i[\rho(t+\tau)\rho_T,\langle V(t+\tau)\rangle_T].$$

Therefore, the expressions (3.2) and (3.3) with the help of Eqs. (2.3), (2.4) and (2.13) get transformed as

$$\begin{aligned} L^{(0)}_{nm}(t) &= i\sum_{n'}[H_{n'n}(t)\gamma_{n'm}(t) - H_{mn'}(t)\gamma_{nn'}(t)],\\ L^{(1)}_{nm}(t) &= i\sum_{n'}[\langle\hat{F}_{n'n}(t)\rangle_T\gamma_{n'm}(t) - \langle\hat{F}_{mn'}(t)\rangle_T\gamma_{nn'}(t)], \end{aligned} \tag{3.4}$$

$$\begin{aligned} L^{(2)}_{nm}(t) = -\sum_{ll'}\sum_{rr'}\int_{-\infty}^{0} d\tau\{&[\langle\Delta\hat{F}_{mr}(t)\Delta\hat{F}^{\tau}_{r'l'}(t+\tau)\rangle_T\gamma_{ll'}(t+\tau)\\ &-\langle\Delta\hat{F}^{\tau}_{l'l}(t+\tau)\Delta\hat{F}_{mr}(t)\rangle_T\gamma_{l'r'}(t+\tau)]\langle r\mid\hat{\gamma}_{r'l}(t;\tau)\mid n\rangle\\ &-[\langle\Delta\hat{F}_{rn}(t)\Delta\hat{F}^{\tau}_{r'l'}(t+\tau)\rangle_T\gamma_{ll'}(t+\tau) - \langle\Delta\hat{F}^{\tau}_{l'l}(t+\tau)\Delta\hat{F}_{rn}(t)\rangle_T\gamma_{l'r'}(t+\tau)]\langle m\mid\hat{\gamma}_{r'l}(t;\tau)\mid r\rangle\}\ , \end{aligned}$$

where

$$\begin{aligned} \Delta\hat{F}^{\tau}_{nm}(t+\tau) &\equiv \exp(iH_T\tau)\Delta\hat{F}_{nm}(t+\tau)\exp(-iH_T\tau),\\ \Delta\hat{F}(t) &\equiv \hat{F}(t) - \langle\hat{F}(t)\rangle_T. \end{aligned} \tag{3.5}$$

Here, the averaging $\langle\hat{A}\rangle_T \equiv \mathrm{Tr}(\rho_T\hat{A})$ over the thermal bath is achieved due to the equilibrium density matrix (2.16) and the Hamiltonian (2.2). The obtained kinetic Eqs. (3.1) and (3.4) are rather general and may describe a number of stochastic field effects. Their greatest advantage is the exact account of the stochastic field in the values $\langle m\mid\hat{\gamma}_{rl}(t;\tau)\mid n\rangle$ of (3.4).

B. Generalized master equation

Our aim is to obtain the closed kinetic equation for the state populations $\gamma_{nn}(t)$ on the basis of the general kinetic equations (3.1) and (3.4). Unfortunately, because of the complicated form of Eqs. (3.1) and (3.4) where diagonal and off-diagonal parameters $\gamma_{nm}(t)$ are strongly coupled, these equations cannot be investigated as a whole. Therefore, in this paper we restrict ourselves to the diagonal stochastic perturbation in the QDS Hamiltonian $H_0(t)$ (2.8) and specific form of the interaction V (2.9).

The choice of the QDS–thermal-bath interaction V [and, respectively, the choice of the operators $\hat{F}_{nm}$ in (2.4)] determines completely the form of the kinetic equations. In the general case, the $n\to m$ transitions in QDS are accompanied by multiphonon transitions in the thermal bath. As a result, relaxation of the state populations $\gamma_{nn}(t)$ interferes with the evolution of the coherences $\gamma_{nm}(t)$. Hence, the off-diagonal effects are significant and one cannot neglect these effects in the kinetic equations for $\gamma_{nn}(t)$. Nevertheless, it was shown in many studies for field-independent cases (see, for example, [27]) that the conditions $|\omega_{nm}| \gg |\langle\hat{F}_{nm}\rangle_T|$ make it possible to obtain the closed kinetic equation for populations $\gamma_{nn}(t)$ on the time scale $\Delta t \gg |\omega_{nm}|^{-1}$ if n and m are nondegenerate levels.

In the presence of the external field the situation is essentially complicated because of the time dependence of QDS levels. Namely, the restriction $|\varepsilon_{nm}(t)| \ll |\omega_{nm}|$ imposed on energetic fluctuations gets appeared. However, one can avoid this restriction by choosing the specific form of the QDS–thermal-bath interaction. Expression (2.9) is one of the possible forms of such an interaction. It reflects the single-phonon approximation when relaxation transitions in QDS are induced by creation and annihilation of the optical phonons with resonant frequencies $\Omega_\lambda \simeq |\omega_{nm}|$. In this case the multiphonon transitions are not important, and we have rigorous decoupling between state populations $\gamma_{nn}(t)$ and coherences $\gamma_{nm}(t)$ in the general kinetic equations (3.1) and (3.4).

To manifest the stochastic field effects let us substitute in the general kinetic equations (3.1) and (3.4) the expressions (2.2),(2.6) and (2.7). To specify the kinetic equations one must take into account that in this case, the values included in (3.4) are given by formulas

$$\begin{aligned} &\langle\hat{F}_{nm}(t)\rangle_T = 0,\quad L^{(0)}_{nm}(t) = i(\omega_{nm}+\varepsilon_{nm}(t)),\\ &L^{(1)}_{nm}(t) = 0,\\ &\langle r\mid\hat{\gamma}_{mm'}(t;\tau)\mid n\rangle\\ &\qquad = \delta_{m'n}\delta_{rm}\exp\left(i\int_t^{t+\tau}\varepsilon_{mm'}(t')dt'\right)\exp[i\omega_{mm'}\tau], \end{aligned} \tag{3.6}$$

$$\begin{aligned} \Delta\hat{F}^{\tau}_{mm'}(t+\tau) &\equiv \Delta\hat{F}^{\tau}_{mm'}\\ &= \exp(iH_T\tau)\Delta\hat{F}_{mm'}\exp(-iH_T\tau), \end{aligned}$$

$$\begin{aligned} \langle\hat{F}^{\tau}_{mn}\hat{F}_{m'n'}\rangle_T &= (\delta_{mm'}\delta_{nn'}+\delta_{mn'}\delta_{nm'})\\ &\quad\times\sum_{\lambda}\mid\kappa^{\lambda}_{nm}\mid^2 R_\lambda(\tau) = \langle\hat{F}_{mn}\hat{F}^{-\tau}_{m'n'}\rangle_T. \end{aligned}$$

According to Eq. (2.7) the average in (3.6) is expressed through the average $\langle B_{\lambda}^{\dagger} B_{\lambda'}\rangle_T$. With the help of Eqs. (2.16) and (2.2) this value is reduced to $\delta_{\lambda\lambda'} N(\Omega_\lambda)$ where

$$N(\Omega_\lambda) = \frac{1}{\exp(\Omega_\lambda / k_B T) - 1} \tag{3.7}$$

is the Bose function. In (3.6) $\varepsilon_{mm'}(t) \equiv \varepsilon_m(t) - \varepsilon_{m'}(t), \omega_{mm'} \equiv \omega_m - \omega_{m'}$, and the value

$$R_\lambda(\tau) = N(\Omega_\lambda) \exp(i\Omega_\lambda \tau) + [1 + N(\Omega_\lambda)] \exp(-i\Omega_\lambda \tau) \tag{3.8}$$

is the relaxation bath function in the one-phonon approximation (2.7). The relations (3.6) reduce the kinetic equations (3.1) and (3.4), specified for the diagonal parameters $\gamma_{nn}(t)$, to the GME at the external field (see also [21,29])

$$\begin{aligned} \frac{\partial}{\partial t}\gamma_{nn}(t) = \mathrm{Re} \sum_m \int_{-\infty}^{0} & d\tau [W_{mn}(\tau) G_{mn} \\ & \times (t+\tau; t) \gamma_{mm}(t+\tau) \\ & - W_{nm}(\tau) G_{nm}(t+\tau; t) \gamma_{nn}(t+\tau) \ . \end{aligned} \tag{3.9}$$

In Eq. (3.9) we introduce the memory function of the thermal bath,

$$W_{mn}(\tau) = 2 \sum_\lambda \mid \kappa_{mn}^{\lambda} \mid^2 R_\lambda(\tau) \exp(i\omega_{mn}\tau) \tag{3.10}$$

and the Green functions

$$G_{mn}(t+\tau; t) = \exp\left(i \int_t^{t+\tau} \varepsilon_{mn}(t') dt' \right) \tag{3.11}$$

for the set of independent Kubo oscillators [8,14,30]. The functions (3.11) reflect the external field influence on the $n \to m$ transitions and obey the equation

$$\frac{\partial}{\partial t} G_{mn}(t; t') = i\varepsilon_{mn}(t) G_{mn}(t; t') \tag{3.12}$$

with the initial condition $G_{mn}(t;t) = 1$.

C. Balancelike equation

Equation (3.9) is a non-Markovian one since the right-hand side is determined by the values of $\gamma_{nn}(t+\tau)$ at $\tau < 0$. However, in some cases this non-Markoviality may be neglected. For example, this is the case of a weak relaxation interaction V when $d\gamma_{nn}(t)/dt \sim V^2$ [20]. It is clear from the expansion

$$\gamma_{nn}(t+\tau) = \gamma_{nn}(t) + \tau \frac{\gamma_{nn}(t)}{dt} = \gamma_{nn}(t) + \sim \tau V^2 \tag{3.13}$$

that non-Markoviality of the right-hand side of (3.9) is significant only in the higher approximations in powers of V . By taking into account the relation (3.13) and the fact that, as a rule, the memory function rapidly falls in time [for instance, in the case of Ohmic thermal bath with phonon bandwidth Γ it falls as $\exp(-\Gamma t)$ [31]] GME (3.9) is simplified to the balancelike equation [generalized Pauli equation (GPE)]

$$\frac{\partial \gamma_{nn}(t)}{\partial t} = \sum_{m \neq n} [w_{mn}(t) \gamma_{mm}(t) - w_{nm}(t) \gamma_{nn}(t)]. \tag{3.14}$$

Equation (3.14) is the linear stochastic equation where the time-dependent coefficients

$$w_{nm}(t) = \mathrm{Re} \int_{-\infty}^{0} d\tau W_{nm}(\tau) G_{nm}(t+\tau; t) \tag{3.15}$$

are stochastic functionals $w_{nm}[\varepsilon_{nm}(t)]$ of the energy fluctuations $\varepsilon_{nm}(t)$.

The stochastic functional (3.15) is completely defined by Eqs. (3.8), (3.10), and (3.11) that provide averaging of the GPE (3.14) over fast stochastic processes.

IV. AVERAGING OVER STOCHASTIC PROCESSES

Let us consider Eq. (3.14) as a stochastic differential equation. The conventional way to make the averaging of the equation over stochastic processes is connected with application of the cumulant expansion method [8,14,30]. The approximation of the first cumulant in terms of the stochastic process $w(t)$ leads to the Pauli equation (1.1), where

$$w_{nm} = \langle w_{nm}(t) \rangle_f = \mathrm{Re} \int_{-\infty}^{0} d\tau W_{nm}(\tau) \langle G_{nm}(\tau; 0) \rangle_f \tag{4.1}$$

is the probability averaged over stationary energy fluctuations. It is necessary to note here that the cumulant expansion may be considered also as an expansion over the Kubo number [8,30,32]

$$K_w = \Delta w \tau_w$$

of the stochastic process $w(t)$. Here the subscript nm is dropped and $\Delta w = \langle [w(t) - w]^2 \rangle_f^{1/2}$ and τ_w are the mean square amplitude and autocorrelation time of the stochastic process $w(t)$, respectively. Equations (1.1) and (4.1) are valid only when $K_w \ll 1$. Proceeding from physical and mathematical viewpoints it is clear that the value Δw cannot be greater than that of average transitional probability w at any arbitrary mean square energy amplitude $\Delta\varepsilon = \langle [\varepsilon(t) - \langle \varepsilon \rangle_f]^2 \rangle_f^{1/2}$ of an original stochastic process $\varepsilon(t)$. Because of this fact the condition $K_w \ll 1$ is fulfilled if $\tau_w \ll w^{-1}$. Further, we assume that the stochastic process $w(t)$ varies on the time scale given by the autocorrelation time τ_ε of the original process $\varepsilon(t)$. From this assumption it follows that the first cumulant approximation in terms of the process $w(t)$ is a good one for very fast energy fluctuation,

$$\tau_\varepsilon \sim \tau_w \ll w^{-1}, \tag{4.2}$$

whereas the Kubo number $K_\varepsilon = \Delta\varepsilon\tau_\varepsilon$ of the original process may be arbitrary. We restrict our consideration to this approximation.

For the purpose of convenience, the expression (4.1) for the average probabilities is written as

$$w_{nm} = \int_{-\infty}^{\infty} d\omega N(\omega) J_{nm}(\omega) I_{nm}(\omega + \omega_{nm}) \tag{4.3}$$

by introducing the thermal-bath spectral function

$$J_{nm}(\omega) = 2\pi \sum_{\lambda} \mid \kappa_{mn}^{\lambda} \mid^2 \delta(\omega - \Omega_\lambda). \tag{4.4}$$

[The function (4.4) is extended on the negative value $\omega < 0$ due to the condition $J_{nm}(-\omega) = -J_{nm}(\omega)$.] The function $J_{nm}(\omega)$ reflects the thermal-bath energy structure as well as its influence on the dynamic system [1,7]. We introduce here also the Kubo line shape function [8,33]

$$I_{nm}(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^{\infty} e^{i\omega\tau} \langle G_{nm}(\tau; 0) \rangle_f d\tau \tag{4.5}$$

which contains all necessary information about the stochastic field influence on the energy levels and may be explicitly found for some kinds of stochastic processes.

It is convenient to simulate a real energy fluctuation by the discrete Markovian kangaroo process (KP) [28,32]. We remind you that a KP is the Markovian process that may take on the discrete random values from the counting set $\{\varepsilon_j\}_{j=1,N}$ with the stationary probabilities $\{p_j\}_{j=1,N}$. It is modified from one value to another by a stationary Poisson sequence with pulse rate $\{\nu(\varepsilon_j)\}_{j=1,N}$ being a function of the current value of the random variable (more detail see [32]). The KP line shape is found easily using the results of Refs. [28,32]. According to them it may be written in the form

$$I(\omega) = \frac{1}{\pi} \mathrm{Re} \left\{ \langle G(\omega + i\nu) \rangle_s + \frac{\langle \nu G(\omega + i\nu) \rangle_s^2}{\langle \nu [1 - \nu G(\omega + i\nu)] \rangle_s} \right\} , \tag{4.6}$$

where $\langle (\cdots) \rangle_s = \sum_{j=1}^{N} p_j (\cdots)_j$ denotes the averaging over the stationary distribution of ε (the subscript nm is dropped). The static resolvent

$$G_j(\omega) = \int_0^{\infty} e^{i\omega t} G_j(t, 0) dt \tag{4.7}$$

in (4.6) is given by Eq. (3.12) with $\varepsilon(t) = \varepsilon_j$. We note that the expression (4.6) is valid at any amplitude and autocorrelation time of the energy fluctuations. The spectral function $J(\omega)$ may be obtained, in any specific case, from *a priori* knowledge of the microscopic interactions, but this function is usually taken in the model form [7]. In fact, the relation (4.3) for average probabilities has the "golden rule" form in which the energy conservation law $\delta(\omega + \omega_{nm})$ is replaced by the line shape function $I(\omega + \omega_{nm})$.

V. TWO-LEVEL SYSTEM IN DICHOTOMOUS FIELD

To manifest the discrete stochastization influence on average probabilities of quantum transitions we consider the two-level system interacting simultaneously with the dichotomous field and the harmonic oscillator that is coupled with the thermal bath. In the coordinate representation the Hamiltonian of the model system is defined as

$$H = [\omega_1 + \varepsilon(t)] \mid 1 \rangle \langle 1 \mid + \omega_2 \mid 2 \rangle \langle 2 \mid + \frac{p^2}{2m_0} + \frac{m_0 \omega_0^2 q^2}{2} + \kappa_0 \sqrt{2 m_0 \omega_0} (\mid 1 \rangle \langle 2 \mid + \mid 2 \rangle \langle 1 \mid) q$$
$$+ \sum_{\lambda} \left[\frac{P_\lambda^2}{2M_\lambda} + \frac{1}{2} M_\lambda \Omega_\lambda^2 \left\{ X_\lambda + \frac{c_\lambda}{M_\lambda \Omega_\lambda^2} q \right\}^2 \right] . \tag{5.1}$$

Here, q and p are the coordinate and momentum of the given oscillator, $\{X_\lambda; P_\lambda\}$ are the coordinates and momenta of the bath oscillators, $m_0, M_\lambda, \omega_0, \Omega_\lambda$ are their masses and frequencies, respectively ; κ_0 and c_λ are the coupling constants and ω_1 and ω_2 are the stationary energy levels of the QDS .

Such a model can be used for the investigation of the bridge mode accompanied charge transfer between sites 1 and 2 that are space separated in the macromolecule [34,35]. Here the intersite bridge mode q may be treated as a reaction coordinate. The rest of the macromolecular modes are considered to be bath modes. The thermal bath is often supposed to be Ohmic. For the Ohmic bath, in the semiclassical limit, the particle moving along the chosen coordinate is exposed to the action of a frictional force linearly proportional to its velocity with a coefficient η [1,36]. In this case, using the results of work [36], the model Hamiltonian (5.1) can be transformed as (2.1), (2.8), and (2.9) with the effective spectral function

$$J(\omega) = 8\kappa_0^2 \frac{\gamma \omega_0 \omega}{(\omega_0^2 - \omega^2)^2 + 4\gamma^2 \omega^2} \tag{5.2}$$

defined according to (4.4). In (5.2) $\gamma = \eta / 2m_0$ is the broadening of oscillator levels. Note that $J(\omega)$ is proportional to the imaginary part of dynamic susceptibility of a damped harmonic oscillator $\chi''(\omega)$ with undamped frequency ω_0 and a friction coefficient η [37],

$$J(\omega) = 4\kappa_0^2 m_0 \omega_0 \chi''(\omega). \tag{5.3}$$

Let us suppose that the fluctuating part of energy $\varepsilon(t)$ is described by the dichotomous Markov process of kangaroo type (DMPK) with the space of realizations $\{\varepsilon_+, \varepsilon_-\}$, jump frequencies $\{\nu_+, \nu_-\}$, and probabilities of realizations $p_+ = \nu_-/(\nu_+ + \nu_-), p_- = \nu_+/(\nu_+ + \nu_-)$. For example, such kinds of fluctuation may be caused by thermal activation of two positional reorientations of the charge molecular group adjacent to site 1. Then the corresponding line shape function may be easily derived using Eqs. (4.6), (4.7), and (3.12). Namely,

$$I(\omega) = \frac{1}{\pi}\frac{(\Delta\varepsilon)^2\nu_c}{(\omega-\varepsilon_+)^2(\omega-\varepsilon_-)^2+(\omega-\bar{\varepsilon})^2\nu_c^2}, \qquad (5.4)$$

where $\bar{\varepsilon} = \langle\varepsilon(t)\rangle_f = (\varepsilon_+\nu_- + \varepsilon_-\nu_+)/(\nu_+ + \nu_-)$ is the average over energy fluctuations and $\Delta\varepsilon = (\nu_+\nu_-)^{1/2}|\varepsilon_+ - \varepsilon_-|/(\nu_+ + \nu_-)$ and $\nu_c = (\nu_+ + \nu_-)/2$ are their mean square amplitude and reverse autocorrelation time, respectively. The expression analogous to (5.3) was obtained earlier by Kubo [33] (in a different way) for DMP. However, DMP is not identical to DMPK. The difference is that in contrast to DMP the DMPK is completely randomized at each jump. This leads to a half reduction of the reverse autocorrelation time of DMPK as compared to DMP. The dependence of $I(\omega)$ on the stochastic process parameters is illustrated in Fig. 1. If the DMPK Kubo number $K_\varepsilon = \Delta\varepsilon/\nu_c$ is small then $I(\omega)$ has a single peaked form at $\omega = \bar{\varepsilon}$. The K_ε increasing leads to the line profile broadening and by $K_\varepsilon = 1/2$ to its splitting. The further increasing of the Kubo number leads to the narrowing of both peaks situated at $\omega = \varepsilon_+$ and $\omega = \varepsilon_-$.

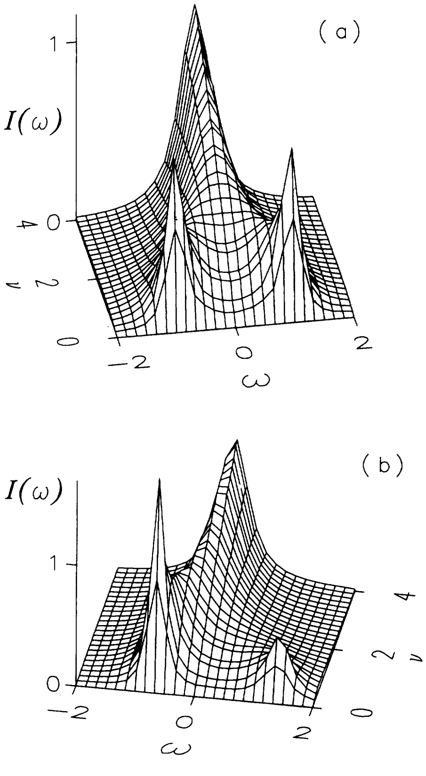

FIG. 1. Dependence of the line form function $I(\omega)$ (in arbitrary units) on frequency ω (in units of $\Delta\varepsilon$) for zero centered dichotomous processes ($\bar{\varepsilon} = 0$) with various reverse autocorrelation times $\nu = (\nu_- + \nu_+)/2$ (in units of $\Delta\varepsilon$) and fixed mean square amplitude $\Delta\varepsilon = (\varepsilon_+\varepsilon_-)^{1/2}$; (a) $\varepsilon_+/\varepsilon_- = 1$, (b) $\varepsilon_+/\varepsilon_- = 2$.

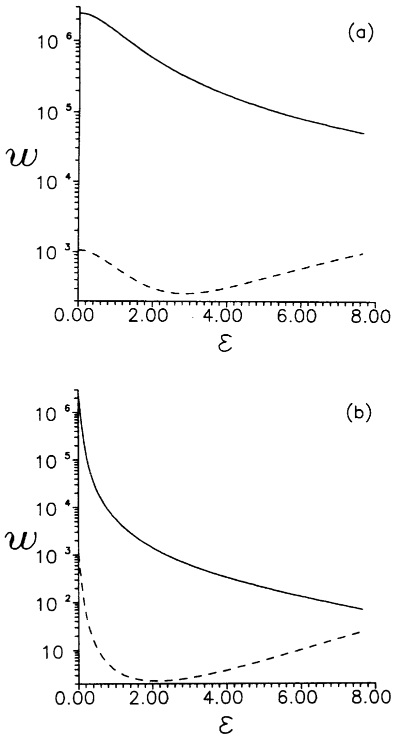

FIG. 2. Dependence of the transition probabilities w_{12} (solid line) and w_{21} (dashed line) in units of s^{-1} on amplitude ε (in units of k_BT) of symmetrical DMPK in the case of (a) weakly colored noise: $K_\varepsilon \ll 1$, $\nu_c = 10^{15}\ \mathrm{s}^{-1}$ and (b) strong colored noise: $K_\varepsilon \gg 1$, $\nu_c = 10^9\ \mathrm{s}^{-1}$; $T = 300$ K, $\omega_{12} = \omega_0 = 3.0 \times 10^{14}\ \mathrm{s}^{-1}$ (~ 0.2 eV), $\gamma = 10\ \mathrm{cm}^{-1}$ ($\sim 1.9 \times 10^{12}\ \mathrm{s}^{-1}$), and $\kappa_0 = 1.0 \times 10^{-6}$ eV ($\sim 1.5 \times 10^{-9}\ \mathrm{s}^{-1}$).

The stochastically averaged transition probabilities w_{12} and w_{21} may be defined now by Eq. (4.3) taking into account Eqs. (3.7), (5.2), and (5.4). The integral in (4.3) can be exactly calculated in analytical form using the theory of residues. Some results of the corresponding numerical calculations are shown in Fig. 2 for the case of symmetrical DMPK ($\varepsilon_+ = -\varepsilon_- = \varepsilon = \Delta\varepsilon, p_+ = p_- = 1/2, \nu_+ = \nu_- = \nu_c$). We stress the sharp dependence of the transition probabilities [and hence the relaxation time $\tau = (w_{12} + w_{21})^{-1}$ in QDS] on the amplitude of fluctuation in the case of strongly colored dichotomous noise ($K_\varepsilon \gg 1$). This changing of the average probabilities under stochastic influence may reach several orders of value.

VI. CONCLUSION

In this paper, we obtained the kinetic equations for a description of the evolution of parameters $\gamma_{nm}(t)$ of a quantum system interacting with thermal bath and discrete stochastic field. Special attention is paid to obtaining the coarse-temporal master equation for the quantum state populations $\langle\gamma_{nn}(t)\rangle_f$ averaged over fast field fluctuations.

GME, (3.9)–(3.11) and GPE [(3.14) and (3.15)] are the main results of this paper. GME and GPE provide for all necessary information about diagonal stochastic effects in the second order term over the bath-system interaction without any quantitative restrictions on possible values of the amplitude and frequency of a stochastic influence. The Pauli equation (1.1) is obtained from GPE in the first cumulant approximation in terms of stochastic processes $w_{nm}(t)$. Such approximation is valid only in the case of very fast stochastic influence $\varepsilon(t)$.

Here we have shown that the $\langle w_{nm}\rangle_f$, averaged over fast process transition probabilities, are sharp nonlinear functions of amplitude ε of energy fluctuations, and they may be changed by several orders of magnitude under the stochastic influence. This fact makes it possible to control transition probabilities through the external stochastic field.

At last, the general kinetic equations (3.1) and (3.4) can be used as a basic equation to study the effects of nondiagonal stochastic and regular perturbations of relaxation processes in the QDS in future investigations.

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