Averaged master equation for a quantum system coupled to a heat bath with fluctuating energy levels

Elmar G. Petrov
Bogolyubov Institute for Theoretical Physics, Ukrainian National Academy of Science, 14-b Metrologichna Street, 252143 Kiev, Ukraine
(Received 19 December 1996; revised manuscript received 7 August 1997)

A master equation for a quantum system coupled to a heat bath with stochastically fluctuating energy levels is derived by making use of the ensemble averaging and the averaging with respect to a stochastic process in the bath. Relaxation terms are determined in the Born approximation with respect to the system-bath interaction and the damping parameters related to a relaxation kernel are specified. In parallel with the spectral strength of the bath, the damping parameters determine the transient times for the Markovian description creating the physical origin of the slippage [A. Suarez, R. Sibey, and I. Oppenheim, J. Chem. Phys. **97**, 5101 (1992)]. The influence of energy fluctuations of the bath is analyzed for a two-level system including the solution of the corresponding non-Markovian equation for the level population difference. The conditions for the formation of Boltzmann's thermal ratio between steady-state populations are evaluated as well. [S1063-651X(97)12612-5]

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

I. INTRODUCTION

In condensed media, the interaction between a quantum system and its environment is the physical factor responsible for relaxation processes in the system. Basic principles of nonequilibrium statistical mechanics [1–7] state that such relaxation processes can be provided by the environment if it acts as a bath.

There exist two distinct models for the bath. The first one identifies the bath with a thermal environment, or a heat bath. In this case, the energy levels of the bath are populated according to the conventional Gibbs distribution. In practice, a heat bath is often simulated by a phonon bath. If the presence of a heat bath has been assumed, the ensemble averaging with respect to bath states is necessary if one derives kinetic equations for the quantum system. Just owing to energy exchange between the system and the heat bath, the density matrix of the system is driven to Gibbs's equilibrium form and the steady-state populations of the energy levels of the system satisfy Boltzmann's equilibrium ratio (if no additional time-dependent external fields act on the system).

In the second model for the bath one provides the existence of random fields created by the environment. Anderson [8] and Kubo [9] proposed the simulation of the random action of the environment introducing random quantities just into the Hamiltonian of the considered quantum system. Later on this idea has been used within the method of the stochastic Liouville equation [5–7,10,11] (see also the discussion of the Haken-Strobl-Reineker method in the theory of exciton transfer [12] as well as the method of stochastic master equation applied in spectroscopy [13]). In contrast to the first model of the bath, the kinetic equations for the quantum system are derived via an averaging with respect to realizations of the random parameters included in the system Hamiltonian. Since this averaging procedure differs from the averaging with respect to a thermal ensemble it leads to principally different results with respect to both relaxation rates and steady-state populations. In particular, the density matrix of the quantum system is not driven to Gibbs's equilibrium form, but to a microcanonical equilibrium density matrix [14]. Furthermore, steady-state populations of the energy levels of the system do not satisfy Boltzmann's equilibrium ratio but become equal to each other.

The ensemble averaging reflects a statistical equilibrium in the heat bath (the equilibrium is kept by the fast energy exchange between the bath and the outside world), whereas the averaging with respect to random processes accounts for an effective dynamic influence of the environment. Both types of averaging may be related to a situation in particular in molecular systems where a widespread set of different motions of the environment appears. Fox [15–17] introduced a combined averaging in the case of a mixed quantum-stochastic bath and derived master equations for the density matrix of the system on the basis of a combined averaging procedure (which includes the ensemble averaging and the averaging with respect to a stochastic process). In particular, he demonstrated in the model of a system coupled stochastically to a phonon reservoir how the quantum system is driven to the thermal equilibrium characterized by Gibbs's density matrix [17]. Later on the combined action of a heat bath and a stochastic field on relaxation processes in a quantum system was studied in somewhat different models [18,19]. In these studies random processes appeared in the fluctuation of the energy levels of the quantum system considered. This second type of stochastic influence leads to somewhat different conclusions. It has been shown that a steady state of the system is not always characterized by Gibbs's density matrix. The result depends on the relation between the coupling of the system to the heat bath and the characteristics of the random processes. However, it is possible to state that the result given in Ref. [17] is definitely correct if the stochastic influence does not lead to a large width of the energy levels of the quantum system.

The present study is devoted to the analysis of relaxation processes proceeding in a quantum system that is coupled to a heat bath, which in turn is the subject of a stochastic influence. The model corresponds to a physical situation where the system (impurities in a crystal, donor-acceptor pairs, etc.) couples to the environment via the nearest surrounding only, which is in thermal and dynamic contact with the remaining environment.

The thermal contact is realized through fast small-amplitude vibrations that create the thermal reservoir. Owing to thermal contact, the phonon system of the surroundings is held in thermal equilibrium and thus appears as a heat bath for the given quantum system. The dynamic contact is associated with large-amplitude nuclear motions that create stochastic fields for the surroundings [20]. As an example, we note that random fields can be created by nonequilibrium degrees of freedom of complex molecular structures (see, e.g., Refs. [21,18] for a general discussion). Here we assume these large-amplitude nuclear motions to be capable of alternating the random dynamic characteristics of the surroundings, in particular, the phonon frequencies of the bath.

The model describing a bath with fluctuating energy levels introduces one more type of stochastic influence on the bath interacting with the outside environment. Earlier, such an influence was considered as the random alternation of the system-bath coupling [17]. Therefore, the present work can be considered as a further investigation of the influence of a quantum-stochastic bath on relaxation processes in a quantum system. In fact, such investigations were initiated with the papers by Faid and Fox [14,17].

II. MODEL AND THEORY

In accordance with the chosen model, we take the Hamiltonian of the whole system (quantum system plus heat bath) as

$$H(t)=H_0(t)+H_B(t)+V, \tag{1}$$

where $H_0(t)$ and $H_B(t)$ are time-dependent Hamiltonians of the system and the bath, respectively, and V denotes a time-independent system-bath interaction. In Ref. [17], the interaction V was assumed to be a stochastic quantity whereas the Hamiltonians H_0 and H_B are taken as time independent. In contrast, in Ref. [18], H_0 was chosen as a stochastically modulated quantity. In the present study, the bath Hamiltonian $H_B(t)$ will be considered as a stochastic value operator, whereas the quantities $H_0(t)$ and V are taken as regular operators. [In $H_0(t)$ a time dependence may appear if a regular time-dependent external field is applied.]

Using the projection operator technique [22,23], we find, in line with Refs. [18,19], the following type of stochastic master equation for the density matrix $\rho(t)$ of the system:

$$\dot{\rho}(t)=-i\hat{L}_0(t)\rho(t)-\hat{L}(\rho(t);t). \tag{2}$$

This equation has been derived within the Born approximation with respect to the interaction V [24], resulting in the following type of relaxation part:

$$\hat{L}(\rho(t);t)=\int_0^t dt'\,\mathrm{Tr}_B\hat{L}_1\hat{S}_0(t,t')\hat{S}_B(t,t')\hat{L}_1\rho_B(H_B^0)\rho(t'). \tag{3}$$

In Eqs. (2) and (3) the Liouville operators $\hat{L}_0(t)\equiv\hbar^{-1}[H_0(t),\ ]$, $\hat{L}_1\equiv\hbar^{-1}[V,\ ]$, and $\hat{L}_B(t)\equiv\hbar^{-1}[H_B(t),\ ]$ are introduced together with the unitary operators

$$\hat{S}_0(t,t')=\hat{T}\exp\left[-i\int_{t'}^{t}d\tau\hat{L}_0(\tau)\right], \tag{4}$$

$$\hat{S}_B(t,t')=\hat{T}\exp\left[-i\int_{t'}^{t}d\tau\hat{L}_B(\tau)\right] \tag{5}$$

and the Gibbs equilibrium matrix of the bath,

$$\rho_B(H_B^0)=\exp(-H_B^0/k_BT)/\mathrm{Tr}_B[\exp(-H_B^0/k_BT)]. \tag{6}$$

The symbol Tr_B in Eqs. (3) and (6) denotes the trace with respect to bath states and the symbol $\hat{T}$ in Eqs. (4) and (5) implies a time ordering. Note that it has been assumed in Eq. (3) that $\langle V\rangle\equiv\mathrm{Tr}_B[\rho_B(H_B^0)V]=0$. Otherwise, the substitutions of H_0 by $H_0+\langle V\rangle$ and of V by $V-\langle V\rangle$ have to be performed in Eqs. (2) and (3).

In deriving the master equation (2) we have assumed that the stochastic influence on the bath energy levels E_a is too weak to result in deviations from the equilibrium density matrix (6). Such an assumption means that the stochastic influence on relaxation processes within the bath [these processes support an equilibrium distribution (6)] is of minor importance and thus the matrix (6) is determined via a stationary Hamiltonian of the bath,

$$H_B^0=\sum_a E_a|a\rangle\langle a|. \tag{7}$$

However, the stochastic influence cannot be ignored in the dynamic matrix (5) with the stochastic Hamiltonian $H_B(t)$. (It is well known that the presence of a stochastic part in the Hamiltonian of a system introduces basic changes in the time evolution of the system [11,25–27]). To specify the stochastic influence of the environment we employ the model of the diagonal stochastic perturbation represented by the stochastic Hamiltonian of the bath

$$H_B(t)=\sum_a [E_a+\varepsilon_a(t)]|a\rangle\langle a|. \tag{8}$$

Here the condition $|E_a|\gg|\varepsilon_a(t)|$ has to be fulfilled for the stochastic time-dependent part $\varepsilon_a(t)$.

To derive from Eq. (2) a noise-averaged master equation it is necessary to specify the type of stochastic process. In addition, a relationship between a typical relaxation time in the quantum system τ_r and the typical characteristic times of the stochastic process must be established. To obtain analytic results we restrict ourself to a dichotomic process [11,25–27] with escape frequencies ν_j [20]. These frequencies determine the realizations of the stochastic part $\varepsilon_a(t)$ in the Hamiltonian (8). Below we suppose fast random realizations of the $\varepsilon_a(t)$ in comparison to relaxation processes within the system. This means that the inverse escape frequencies ν_j^{-1} of a given discrete stochastic process satisfy the condition $\tau_r\gg\nu_j^{-1}$. Such a supposition justifies the decoupling procedure

$$\langle\langle \hat{S}_B(t,t')\hat{L}_1\rho_B(H_B^0)\rho(t')\rangle\rangle = \langle\langle \hat{S}_B(t,t')\hat{L}_1\rho_B(H_B^0)\rangle\rangle \times\langle\langle \rho(t')\rangle\rangle, \qquad (9)$$

which will be carried out in the relaxation term (3) as the result of averaging with respect to the fast stochastic process (noise averaging is denoted via $\langle\langle\ \rangle\rangle$). More precisely, the decoupling is valid since the relaxation behavior of the density matrix of the system $\rho(t)$ is characterized by the time scale of the relaxation process of order $\Delta t \sim \tau_r$, whereas the characteristic time scale of a random process contained in $\hat{S}_B(t,t')$ is ν_j^{-1}.

Introducing the abbreviation $\sigma(t)\equiv\langle\langle\rho(t)\rangle\rangle$ and using Eqs. (2), (3), and (9), one finds the following noise-averaged master equation for the system:

$$\dot{\sigma}(t) = -\frac{i}{\hbar}[H_0(t),\sigma(t)] - \frac{1}{\hbar^2}\int_0^t dt' \mathrm{Tr}_B([V,\hat{S}_0(t,t') \times\langle\langle \hat{S}_B(t,t')\rangle\rangle[V,\rho_B(H_B^0)\sigma(t')]]). \qquad (10)$$

To obtain the averaged kernel we rewrite it in a tetradic representation by choosing a complete basis $|n\rangle$ of system states. Then the Hamiltonian $H_0(t)$ and the interaction V can be expressed by the transition operators $\hat{\gamma}_{nm}\equiv|n\rangle\langle m|$ [4,27],

$$H_0(t) = \sum_{m,n} H_{mn}(t)\hat{\gamma}_{mn}, \quad V = \sum_{m,n} \hat{F}_{mn}\hat{\gamma}_{mn}. \qquad (11)$$

Here $H_{mn}(t) = \langle m|H_0(t)|n\rangle$ are the matrix elements of the system Hamiltonian, whereas the quantities $\hat{F}_{mn} = \langle m|V|n\rangle$ are operators resulting from the system-bath coupling. These operators act in the basis set given by the Hamiltonian (7). Each operator $\hat{F}_{mn}$ represents a process in which transitions within the bath are accompanied by the transition of the system from state n to state m. With Eq. (11) the tetradic representation reads

$$\dot{\sigma}_{mn}(t) = -\frac{i}{\hbar}\sum_{m'} \{H_{mm'}(t)\sigma_{m'n}(t) - H_{m'n}(t)\sigma_{mm'}(t)\} - \sum_{m',n'}\int_0^t \Gamma_{mn;m'n'}(t,t')\sigma_{m'n'}(t')dt'. \qquad (12)$$

The matrix elements

$$\Gamma_{mn;m'n'}(t,t') = \frac{1}{\hbar^2}\sum_{r,r'} \{K_{mr;r'm'}(t,t')S_{rn;r'n'}(t,t') + K^*_{rn;n'r'}(t,t')S_{mr;m'r'}(t,t') - K_{rn;r'm'}(t,t')S_{mr;r'n'}(t,t') - K^*_{mr;n'r'}(t,t')S_{rn;m'r'}(t,t')\} \qquad (13)$$

of the relaxation supermatrix $\Gamma(t,t')$ are expressed via the matrix elements

$$S_{mn;m'n'}(t,t') = \langle m|S_0(t,t')\hat{\gamma}_{m'n'}|n\rangle \qquad (14)$$

of the dynamic matrix (4) and the correlation functions

$$K_{mn;m'n'}(t,t') = \mathrm{Tr}_B[\rho_B(H_B^0)\hat{F}_{mn}\langle\langle \hat{S}_B(t,t')\hat{F}_{m'n'}\rangle\rangle], \qquad (15)$$

which specify the bath response.

To evaluate the correlation functions (15) we additionally expand the operator $\hat{F}_{mn}$ with respect to a complete basis set $|a\rangle$ of the bath Hamiltonian (7),

$$\hat{F}_{mn} = \sum_{a,b} \langle a|\hat{F}_{mn}|b\rangle|a\rangle\langle b|. \qquad (16)$$

Then, using Eqs. (6)–(8) and (16), one finds

$$K_{mn;m'n'}(t,t') = \frac{1}{Z}\sum_{a,b} \exp[-E_b/k_BT]\langle b|\hat{F}_{mn}|a\rangle\langle a|\hat{F}_{m'n'}|b\rangle \times X_{ab}(t,t')\exp[i(E_a-E_b)(t-t')/\hbar], \qquad (17)$$

where $Z = \Sigma_a \exp[-E_a/k_BT]$ is the bath state sum. The stochastic properties of the environment are contained in the quantity

$$X_{ab}(t,t') = X^*_{ba}(t,t') = \left\langle\left\langle \exp\left[\frac{i}{\hbar}\int_t^{t'}[\varepsilon_a(\tau)-\varepsilon_b(\tau)]d\tau\right]\right\rangle\right\rangle, \qquad (18)$$

which depends on the type of the bath fluctuations $\varepsilon_a(t)$ and on the specificity of matrix elements $\langle b|\hat{F}_{mn}|a\rangle$ for each pair of system states (mn).

In the case of a dichotomic random process the averaging can be performed exactly. We illustrate this fact by analyzing a typical model of the bath defined as the set of quantum harmonic oscillators with frequencies $\omega_\lambda(t) = \omega_\lambda + \Delta\omega_\lambda(t)$, where $\Delta\omega_\lambda(t)$ is a stochastic contribution to the frequency ω_λ. The operator $\hat{F}_{mn}$ initiates transitions between bath states $|a\rangle = |\{n_\lambda\}\rangle$ and $|b\rangle = |\{n'_\lambda\}\rangle$ with definite sets of population numbers $\{n_\lambda\}$ and $\{n'_\lambda\}$. The energy differences in Eqs. (17) and (18) read, respectively,

$$E_a - E_b = \hbar\sum_\lambda (n_\lambda - n'_\lambda)\omega_\lambda,$$

$$\varepsilon_a(t) - \varepsilon_b(t) = \hbar\sum_\lambda (n_\lambda - n'_\lambda)\Delta\omega_\lambda(t). \qquad (19)$$

Any frequency fluctuation $\Delta\omega_\lambda(t)$ in a dichotomous process has only two realizations $\Delta\omega_{\lambda 1}$ and $\Delta\omega_{\lambda 2}$ characterized by two escape frequencies $\nu_{\lambda 1}$ and $\nu_{\lambda 2}$. Utilizing the method of Brissaud and Frish [26] and following Ref. [18] one gets

$$X_{ab}(t,t') = X_{ab}(t-t') = \prod_\lambda X(n_\lambda, n'_\lambda; t-t'),$$

$$X(n_\lambda, n'_\lambda; \tau) = e^{-i\overline{\Delta\Omega}_\lambda \tau}\frac{1}{\widetilde{\omega}_{1\lambda} - \widetilde{\omega}_{2\lambda}} \times[\widetilde{\omega}_{1\lambda}e^{-\widetilde{\omega}_{2\lambda}\tau} - \widetilde{\omega}_{2\lambda}e^{-i\widetilde{\omega}_{1\lambda}\tau}]. \qquad (20)$$

The averaged frequency contributions $\overline{\Delta\Omega}_\lambda$ are originated by the stochastic process, together with the complex frequencies $\widetilde{\omega}_{j\lambda}\equiv\Omega_{j\lambda}-i\gamma_{j\lambda}$. These quantities read

$$\overline{\Delta\Omega}_\lambda=\frac{\nu_{\lambda 1}\Delta\omega_{\lambda 2}+\nu_{\lambda 2}\Delta\omega_{\lambda 1}}{\nu_{\lambda 1}+\nu_{\lambda 2}}(n_\lambda-n'_\lambda); \qquad (21)$$

$$\Omega_{j\lambda}=\frac{1}{2}\left[\alpha_{1\lambda}-\alpha_{2\lambda}-(-1)^j\xi_\lambda\sin\frac{\varphi_\lambda}{2}\right],$$

$$\gamma_{j\lambda}=\frac{1}{2}\left[\nu_\lambda-(-1)^j\xi_\lambda\cos\frac{\varphi_\lambda}{2}\right], \qquad (22)$$

where

$$\xi_\lambda=\{[\nu_\lambda^2-(\alpha_{1\lambda}+\alpha_{2\lambda})^2]^2+4\nu_\lambda^2(\alpha_{1\lambda}-\alpha_{2\lambda})^2\}^{1/4},$$

$$\nu_\lambda=\frac{1}{2}(\nu_{\lambda 1}+\nu_{\lambda 2}), \qquad (23)$$

$$\tan\varphi_\lambda=\frac{2\nu_\lambda(\alpha_{1\lambda}-\alpha_{2\lambda})}{|\nu_\lambda^2-(\alpha_{1\lambda}+\alpha_{2\lambda})^2|},$$

$$\alpha_{j\lambda}\equiv-(-1)^j[\Delta\omega_{\lambda j}(n_\lambda-n'_\lambda)-\overline{\Delta\Omega}_\lambda]. \qquad (24)$$

Equations (22) are valid if $\nu_\lambda^2\geqslant(\alpha_{1\lambda}+\alpha_{2\lambda})^2$ and $\pi/2\geqslant\varphi_\lambda\geqslant 0$. If $\nu_\lambda^2\leqslant(\alpha_{1\lambda}+\alpha_{2\lambda})^2$ one has to substitute φ_λ by $\pi-\varphi_\lambda$.

III. APPLICATION TO A TWO-LEVEL SYSTEM

The exact expressions (21)–(24) clearly show the appearance of a particular damping mechanism in the relaxation supermatrix $\Gamma(t,t')$ in addition to the damping resulting from the spectral strength for the bath $J(\omega)$. This spectral strength is determined by the correlator related to the coupling of the system to the bath (see examples in Refs. [7,5,6,18,29]). To compare both mechanisms we consider a two-level system by choosing the spin-boson model [30]. In the basis set $|\pm\rangle$ that diagonalizes the two-level Hamiltonian H_0 and leads to a transformation in the system-bath interaction V, Eqs. (11) reduce to the form $H_0=-(\hbar\Delta/2)\hat{\sigma}_z$ and $V=\hat{F}\hat{\sigma}_x$. Here $\hat{\sigma}_z=\hat{\gamma}_{++}-\hat{\gamma}_{--}$ and $\hat{\sigma}_x=\hat{\gamma}_{+-}+\hat{\gamma}_{-+}$ are Pauli-matrices, whereas $-\hbar\Delta/2=H_{++}=-H_{--}$ and $\hat{F}\equiv\hat{F}_{+-}=\hat{F}_{-+}$ are the eigenvalues of the system Hamiltonian and the coupling operator $\hat{F}$, respectively. Below we take the operator $\hat{F}$ in the standard form of a linear coupling between the bath and the system,

$$\hat{F}=\hbar\sum_\lambda \kappa_\lambda(b_\lambda+b_\lambda^\dagger). \qquad (25)$$

In Eq. (25), κ_λ is the coupling to the λth bath mode and b_λ ($b_\lambda^\dagger$) is the annihilation (creation) operator of this mode. With Eq. (25) one finds the nonvanishing correlation functions (17)

$$\begin{aligned}K_{+-;+-}(t,t')&=K_{-+;-+}(t,t')=K_{+-;-+}(t,t')\\&=K_{-+;+-}(t,t')\equiv K(t-t')\\&=\sum_\lambda \kappa_\lambda^2\{n(\omega_\lambda)X_{\lambda-}(t-t')e^{i\omega_\lambda(t-t')}\\&\quad+[1+n(\omega_\lambda)]X_{\lambda+}\\&\quad\times(t-t')e^{-i\omega_\lambda(t-t')}\},\end{aligned} \qquad (26)$$

where the abbreviation $X_{\lambda\pm}(\tau)\equiv X(n_\lambda,n_\lambda\pm 1;\tau)$ has been introduced. In contrast to these rather complex expressions the matrix elements (14) are given by simple expressions

$$S_{++;++}(t,t')=S_{--;--}(t,t')=1,$$

$$S_{+-;+-}(t,t')=S^*_{-+;-+}(t,t')=e^{-i\Delta(t-t')}. \qquad (27)$$

In the framework of the spin-boson model the quantity $X_{\lambda\pm}(\tau)$ is independent of population numbers n_λ. Therefore, a kinetic equation for the Bloch vector with components $z(t)=\sigma_{++}(t)-\sigma_{--}(t)$, $x(t)=\sigma_{+-}(t)+\sigma_{-+}(t)$, and $y(t)=i[\sigma_{+-}(t)-\sigma_{-+}(t)]$ can be easily derived from the generalized master equation (12). For instance, the kinetic equation for the population difference reads

$$\begin{aligned}\dot{\sigma}_z(t)=&-\int_0^t[\Gamma_1(\tau)+\Gamma_2(\tau)]\sigma_z(t-\tau)d\tau\\&+\int_0^t[\Gamma_2(\tau)-\Gamma_1(\tau)]d\tau,\end{aligned} \qquad (28)$$

where the kernels

$$\Gamma_1(\tau)=K(\tau)e^{i\Delta\tau}+K(-\tau)e^{-i\Delta\tau},$$

$$\Gamma_2(\tau)=K(\tau)e^{-i\Delta\tau}+K(-\tau)e^{i\Delta\tau} \qquad (29)$$

specify the relaxation properties of the bath.

According to the mentioned condition $|E_a|\gg|\varepsilon_a(t)|$ of a weak stochastic modulation of the bath energy levels, the correlation function (26) can be expressed via the spectral strength of the bath

$$J(\omega)=2\pi\sum_\lambda \kappa_\lambda^2\delta(\omega-\omega_\lambda) \quad (\omega\geqslant 0), \qquad (30)$$

as

$$\begin{aligned}K(\tau)=K_0(\tau)=\frac{1}{2\pi}\int_0^\infty&\{n(\omega)e^{i\omega\tau}\\&+[1+n(\omega)]e^{-i\omega\tau}\}J(\omega)d\omega.\end{aligned} \qquad (31)$$

Choosing an appropriate model for $J(\omega)$, one can estimate the damping properties of the kernels in Eq. (29). In the case of the Debye bath the spectral strength has the form [29]

$$J(\omega)=\eta(\omega^3/\omega_c^2)\exp[-(\omega/\omega_c)], \qquad (32)$$

where η is a dimensionless friction constant and ω_c is a cutoff frequency. Expression (32) shows that at $\tau\omega_c \gg 1$ the asymptotic behavior of $K(\tau)$ is proportional to τ^{-4}. Hence a nonexponentional decrease of the kernels (29) on the time scale $\Delta\tau \sim \omega_c^{-1}$ appears. To obtain an exponential decrease a particular type of $J(\omega)$ with complex poles has to be constructed. Such a type is beyond the standard spin-boson model.

However, an exponentional decay of the kernels (29) follows from the present alternation of the spin-boson model since a stochastic modulation of the bath levels has been assumed. It is precisely the functions $X_{\lambda\pm}(\tau)$ that reflect the exponential decay of the kernels via the damping parameters $\gamma_{j\lambda}$ [Eq. (22)]. At large Kubo numbers [11,25] $K_{j\lambda} \equiv \alpha_{j\lambda}^{-1}\nu_{j\lambda} \gg 1$ the averaged quantities $X_{\lambda\pm}(\tau)$ take a simple form

$$X_{\lambda\pm}(\tau) = e^{\pm i\overline{\Delta\Omega}_\lambda \tau} e^{-\gamma_\lambda|\tau|}. \tag{33}$$

The stochastic field-induced quantities

$$\overline{\Delta\Omega}_\lambda = \frac{\nu_{\lambda 1}\Delta\omega_{\lambda 2} + \nu_{\lambda 2}\Delta\omega_{\lambda 1}}{\nu_{\lambda 1} + \nu_{\lambda 2}},$$

$$\gamma_\lambda = \frac{\alpha_{1\lambda}\alpha_{2\lambda}}{\nu_\lambda} = \frac{2\nu_{\lambda 1}\nu_{\lambda 2}}{(\nu_{\lambda 1}+\nu_{\lambda 2})^3}(\Delta\omega_{\lambda 1} - \Delta\omega_{\lambda 2})^2 \tag{34}$$

are responsible for the specific contribution in the correlation functions (33) and (26). Due to our basic assumption $\omega_\lambda \gg |\Delta\omega_{\lambda j}|$, one can omit the frequency renormalization $\Delta\Omega_\lambda$ in comparison to ω_λ. Of course, the damping parameters γ_λ have to be considered since they ensure an exponential decrease of the kernels (29).

If a weak dependence of the damping parameters γ_λ on λ is provided, the correlation functions (26) can be approximated as

$$K(\tau) = e^{-\gamma|\tau|}K_0(\tau), \tag{35}$$

where $K_0(\tau)$ is determined via the spectral strength of the bath [see Eqs. (30) and (31)]. Now a single quantity $\gamma \approx \gamma_\lambda$ characterizes the influence of the stochastic processes initiated by the environment.

Expression (35) manifests the appearance of a damping parameter γ in the correlation function related to the bath response. In particular, the presence of γ justifies a Markovian approximation in the kinetic equation (28) if this parameter far exceeds the reverse relaxation time τ_r of the system where $\tau_r^{-1} \sim V^2$. To justify this statement we present an exact solution of the integro-differential kinetic equation (28). This will be done for the Laplace-transform $\tilde{\sigma}_z(p) = \int_0^\infty \exp(-pt)\sigma_z(t)dt$ and in the case of a single bath mode with frequency ω_0. Therefore, we set

$$J(\omega) = 2\pi\kappa_0^2\delta(\omega - \omega_0) \tag{36}$$

and obtain the solution

$$\tilde{\sigma}_z(p) = \frac{\sigma_z(0)p\{[(p+\gamma)^2+\Delta^2+\omega_0^2]^2 - 4\Delta^2\omega_0^2\} - 8\kappa_0^2\Delta\omega_0(p+\gamma)}{p(p\{[(p+\gamma)^2+\Delta^2+\omega_0^2]^2 - 4\Delta^2\omega_0^2\} + 4\kappa_0^2[2n(\omega_0)+1][(p+\gamma)^2+\Delta^2+\omega_0^2](p+\gamma))}. \tag{37}$$

Returning to the time domain, this expression leads to the following asymptotic behavior of $\sigma_z(t)$:

$$\sigma_z(t) = [\sigma_z(0) - \sigma_z(\infty)]\exp(-t/\tau_r) + \sigma_z(\infty). \tag{38}$$

Here the rate constant

$$k \equiv \tau_r^{-1} = 2\kappa_0^2[2n(\omega_0)+1] \times \left[\frac{\gamma}{\gamma^2+(\Delta-\omega_0)^2} + \frac{\gamma}{\gamma^2+(\Delta+\omega_0)^2}\right] \tag{39}$$

and the steady-state population difference

$$\sigma_z(\infty) = \lim_{p\to 0} p\tilde{\sigma}_z(p) = -\frac{2\Delta\omega_0}{[2n(\omega_0)+1](\gamma^2+\Delta^2+\omega_0^2)} \tag{40}$$

correspond to a Markovian approximation that follows immediately from Eq. (28) if one sets $\sigma_z(t-\tau) \approx \sigma_z(t)$ and shifts the upper integral limit to ∞. The Markovian approximation also follows from an exact solution of Eq. (37) if the single damping parameter γ is kept in the term $p+\gamma$. At $|p| \ll \gamma$, the quantity $\tilde{\sigma}_z(p)$ has only two poles, $p=0$ and $p=-\tau_r^{-1}$, and thus the condition $\gamma\tau_r \gg 1$ for the applicability of a Markovian approximation is justified.

The rate constant (39) and the steady-state population difference (40) depend on dynamic (Δ and ω_0), statistical ($n(\omega_0) = [\exp(\hbar\omega_0/k_BT) - 1]^{-1}$), and stochastic ($\gamma$) characteristics of the system and the bath. At a minor stochastic influence, i.e., if $\gamma \ll \Delta, \omega_0$, the maximum of the rate constant is reached at $\Delta \approx \omega_0$. For the same condition, the Boltzmann ratio $\exp(-\hbar\Delta/k_BT) \approx \exp(-\hbar\omega_0/k_BT)$ between steady populations $N_1 = (1/2)[1+\sigma_z(\infty)]$ and $N_2 = (1/2)[1-\sigma_z(\infty)]$ is fulfilled. In the opposite limit where $\gamma \gg \Delta, \omega_0$, the rate (39) is proportional to κ_0^2/γ, whereas the steady-state populations are equal to one another. However, this limiting case is hardly met in physical systems, which becomes obvious from the following estimations. Vibrational frequencies in condensed-matter systems do not exceed several hundred cm^{-1} and hence we may set $\omega_0 \sim 10^{12} - 10^{13}\ \text{s}^{-1}$. The escape frequencies ν_j of the stochastic field can be chosen at the same order of magnitude. To get large Kubo numbers we take the frequency modulation of Eq. (19) as $\Delta\omega_\lambda(t) \sim 10^{11} - 10^{12}\ \text{s}^{-1}$. With $\gamma \approx \gamma_\lambda$, given in Eq. (34), one finds $\gamma \sim 10^{10} - 10^{11}$ s^{-1}, i.e., γ is far below the single frequency ω_0.

IV. CONCLUDING REMARKS

The results of the present study demonstrate the particular properties of a damping process in a quantum system that is in contact with a heat bath formed by the nearest structural groups of the environment. The remaining part of the environment serves as a macroscopic thermal reservoir and, additionally, as a source of stochastic fields. Just these random fields are assumed to be responsible for stochastic fluctuations in the bath. Due to the stochastically fluctuating energy levels of the bath, a specific damping process appears in the master equation for the quantum system. Despite the fact that the corresponding damping parameters $\gamma_{j\lambda}$, given in Eq. (22), are independent of the system-bath interaction V, the appearance of these parameters in the relaxation kernels (13), (17), and (18) [or more simple kernels (29), (35)] can significantly modify the solution of the averaged master equation (12) [or the kinetic equation (28) for a two-level system]. In particular, one can reduce the non-Markovian master equation to a Markovian equation of the Redfield type [28]. With respect to the results of Oppenheim *et al.* [7,29], such a reduction is valid only after some transient time of the order of the relaxation time within the bath. Our study shows that the quantities $\gamma_{j\lambda}^{-1}$ can serve as the above-mentioned transient times. Additionally, the presence of damping parameters $\gamma_{j\lambda}$ in the relaxation term of the master equation in parallel to the spectral strength (30) of the bath creates a particular foundation for the slippage (modification of the initial conditions upon which the generator for the Markovian evolution acts [29]). It should be mentioned here that the necessary conditions for a slippage can be found also in the model of a stochastic system-bath coupling [17] since the corresponding autocorrelations exhibit an exponentional decay in time.

ACKNOWLEDGMENTS

This work was supported by the International Soros Science Education Program through Grants Nos. SPU 062047 and 072048 and by the Fund of Fundamental Researches of the Ukrainian Ministry for Science and Technology through Project No. 2.4/625.

[1] S. Fujita, *Introduction to Non-Equilibrium Quantum Statistical Mechanics* (Saunders, Philadelphia, 1966).

[2] D.N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Plenum, New York, 1974).

[3] A.I. Akhiezer and S.V. Peletminskii, *Methods of Statistical Physics* (Pergamon, London, 1981).

[4] V.G. Bar'yakhtar and E.G. Petrov, *Kinetic Phenomena in Solids* (Naukova Dumka, Kiev, 1989).

[5] K. Lindenberg and B.J. West, *The Nonequilibrium Statistical Mechanics of Open and Closed Systems* (VCH, New York, 1990).

[6] U. Weiss, *Quantum Dissipative Systems*, Series in Modern Condensed Matter Physics Vol. 2 (World Scientific, Singapore, 1993).

[7] I. Oppenheim, K.E. Shuler, and G.H. Weiss, *Stochastic Processes in Chemical Physics: The Master Equation* (MIT Press, Cambridge, MA, 1977).

[8] P.W. Anderson, J. Phys. Soc. Jpn. **9**, 888 (1954).

[9] R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).

[10] R. Kubo, J. Phys. Soc. Jpn. **26**, 1 (1969).

[11] N.G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1984).

[12] V.M. Kenkre and P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates* (Springer, Berlin, 1982).

[13] P.A. Apanasevich, S. Ya. Kilin, and A.P. Nizovtsev, J. Appl. Spectrosc. **47**, 1213 (1988).

[14] K. Faid and R.F. Fox, Phys. Rev. A **34**, 4286 (1986).

[15] R.F. Fox, J. Math. Phys. **17**, 1148 (1976).

[16] R.F. Fox, Phys. Rep. **48**, 179 (1978).

[17] K. Faid and R.F. Fox, Phys. Rev. A **35**, 2684 (1987).

[18] E.G. Petrov, I.A. Goychuk, and V. May, Phys. Rev. E **54**, 4726 (1996).

[19] E.G. Petrov, I.A. Goychuk, and V. May, Physica A **233/1-2**, 560 (1996).

[20] Stochastic fields created by high-amplitude nuclear motions manifest the rearrangement of molecular groups in a given environment. Therefore, such fields can be characterized by mean lifetimes τ_j (or mean escape frequencies $\nu_j = \tau_j^{-1}$) of molecular groups related to the mean times they spent in certain sites j [18].

[21] R.D. Astumian, P.B. Chock, T.Y. Tsong, and H.V. Westerhoff, Phys. Rev. A **39**, 6416 (1989); T.Y. Tsong and R.D. Astumian, Prog. Biophys. Mol. Biol. **50**, 1 (1987).

[22] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).

[23] P.N. Argyres and P.L. Kelley, Phys. Rev. **134**, A97 (1964).

[24] To derive a Born approximation from a general form of the stochastic master equation one has to be sure that V is in fact a small perturbation. To find a perturbation V in a concrete physical system, the given system has to be divided in such a manner that a chosen quantum system and a heat bath become well separated from one another, i.e., a mixture between degrees of freedom of the system and the bath caused by an interaction V has to be rather weak.

[25] R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburg, 1962); Adv. Chem. Phys. **15**, 101 (1969).

[26] A. Brissaud and U. Frish, J. Quant. Spectrosc. Radiat. Transf. **11**, 1767 (1971).

[27] E.G. Petrov, V.I. Teslenko, and I.A. Goychuk, Phys. Rev. E **49**, 3894 (1994); I.A. Goychuk, E.G. Petrov, and V. May, *ibid.* **51**, 2982 (1995).

[28] A.G. Redfield, Adv. Magn. Reson. **1**, 1 (1965).

[29] A. Suarez, R. Silbey, and I. Oppenheim, J. Chem. Phys. **97**, 5101 (1992).

[30] A.J. Legget, S. Chakravarty, A. Dorsey, M.P.A. Fisher, A. Carg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).