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KINETICS IN THE TWO-LEVEL SYSTEM WITH STRONG TIME-DEPENDENT COUPLING OF ITS STATES TO THE PHONON BATH: SPIN-BOSON DESCRIPTION

Using the methods of nonequilibrium statistical mechanics, the master equation for the density matrix of an open dissipative quantum system is obtained under conditions, when the coupling between the electronic states of the system and the nuclear displacements in it is controlled by the alternating field. A time-dependent polaron transformation is proposed, which made it possible to solve kinetic equations using an expansion in a parameter characterizing transitions between "phonon-dressed" electronic states of the system. As an example, a mechanism is shown that can control the kinetics in a two-level system by applying a periodic force field to electron-phonon coupling.

Keywords: quantum kinetics, two-level system, spin-boson model.

1. Introduction

Kinetic processes play a fundamental role in the temporal behavior of a dynamical system, when the system is driven by external regular/stochastic fields [1–3, 6, 7]. The most complete description of the kinetics is possible using methods of nonequilibrium statistical mechanics adapted for open systems [1, 2, 4, 5, 8–11]. One of them is a two-level system (TLS), which is widely used as a model to explain non-stationary processes in condensed matter. It is shown that if a TLS interacts with vibrations of structural groups of the environment, then the temporary behavior of such a system can be conveniently analyzed using the spin-boson approach [12, 13]. The latter has shown its high efficiency in describing kinetic processes in TLS controlled by random/regular electric fields (see examples in refs. [14–18] and when studying electron transfer along a molecular wire [19].

The establishment of stationary characteristics of the dynamic system occurs due to relaxation caused by the interaction of the system with the environment. With a weak coupling between the electronic degrees of freedom of the system and the vibrational degrees of freedom of the environment, the kinetics can be described by the Redfield equations for the elements of the density matrix of the system. With a strong coupling, a noticeable change in the rates of transition between system states occurs, and the Pauli equations for the probabilities of population of system states are used to describe the kinetics. For TLS, these issues are analyzed in detail in Ref. [16]. It was assumed that the coupling between the indicated degrees of freedom does not depend on time, and, therefore, the kinetic equations contain time-independent transition rates. The appearance of rate constants is possible, if the equilibrium position of the nuclei of the system and/or environment does not change with time, and only small displacements of the nuclei from the equilibrium position occur. If this is not the case, the coupling between the electronic and nuclear degrees of freedom becomes time-dependent. It is shown that, under a weak system-environment coupling, this leads to Redfield-type kinetic equations with time-dependent transition rates. [16,20]. As for dynamic systems with a strongly time-dependent coupling, to the best of the authors' knowledge, the corresponding kinetic equations have not yet been obtained.

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The goal of this work is to obtain kinetic equations and corresponding rates characterizing transitions between TLS states that are strongly coupled to the vibrational degrees of freedom of the environment. It is shown that, due to the time dependence of the noted coupling, the electronic states of the system manifest themselves as polarons with a nonstationary "phonon coat".

2. Model and Basic Equations

We will consider an open dynamic quantum system S, in which the nuclear equilibrium position q_{0n}, associated with the motion along the normal coordinate q, depends on the nth electronic state of the system. The system S interacts with the environment E, which does not change its electronic state. So, each jth equilibrium position of the nuclei Q_{0j} corresponds to the jth normal coordinate of the motion in a fixed electronic state of the environment. It is assumed that the nuclei in system S and in E have small deviations Δq_n and ΔQ_j from their equilibrium positions, so that, in the harmonic approximation, the noted deviations are characterized by the corresponding frequencies ω_n and ω_j.

2.1. Hamiltonian of the entire $S + E$ system

The main features of the temporal behavior of an open quantum dynamical system are determined by the relations between the matrix elements $V_{nn'}$ of transitions between the electronic states of the system and the couplings κ_n of each nth state to vibrational states of the environment. The influence of external *dc* and *ac* fields is taken into account, as a rule, in the energies $E_n = E_n(t)$ of the system and quantities $V_{nn'} = V_{nn'}(t)$. In this work, we focus on the situation when the kinetics in an open system is controlled by the couplings $\kappa_n(t)$ (caused, for example, by external forces) [16, 22]. Having expanded the energy into small deviations Δq_n and ΔQ_j, after introducing the Bose operators of creation (b_j^+) and annihilation (b_j) of the phonon mode j for the environment and similar operators (b^+ and b) for a single mode of a dynamical system, we arrive at the following form of the Hamiltonian for the entire system $S + E$:

$$H_{\rm SE}(t) = \sum_{n,n'} \Big\{[E_n(t) + \kappa_n(t)(b^+ + b) + \\ + \hbar\omega_n(b^+ b + 1/2) + \sum_j \kappa_{nj}(b_j^+ + b_j)]\delta_{n,n'} + \\ + (1-\delta_{n,n'})V_{nn'}(t)\Big\}|n\rangle\langle n'| + \sum_j \hbar\omega_j(b_j^+ b_j + 1/2). \quad (1)$$

To describe the kinetics in an open system, it is important to specify which states of the Hamiltonian (1) mainly take part in the time evolution for given physical parameters of the S + E system. To this end, using the method of Bogolyubov's time hierarchies [1, 2] we will consider possible characteristic times of transient processes in the entire S + E system. Let $\tau_{\rm tr}$ be the characteristic time of a kinetic process responsible for the establishment of a stationary regime in S, and $\tau_{\rm rel}$ is the characteristic time at which the Boltzmann distribution within the vibrational levels of electronic terms is maintained in both systems E and S. Besides, there exists also the characteristic time $\tau_{\rm field} \sim \omega^{-1}$ related to the oscillations of an external *ac* field with frequency ω.

In this work, we consider the kinetics on a time scale of the order of $\Delta t \sim \tau_{\rm tr}$, satisfying the inequalities

$$\tau_{\rm tr} \gg \tau_{\rm field} \gg \tau_{\rm rel}. \quad (2)$$

This means that we are studying coarse-grained kinetics, where vibrational levels can be attributed to a heat bath with a Hamiltonian

$$H_{\rm B} = \sum_\lambda \hbar\omega_\lambda(b_\lambda^+ b_\lambda + 1/2). \quad (3)$$

The corresponding equilibrium density matrix of the bath is $\rho_{\rm B} = \exp(-H_{\rm B}/k_{\rm B}T)/{\rm Tr}\exp(-H_{\rm B}/k_{\rm B}T)$ ($k_{\rm B}$ and T are the Boltzmann constant and temperature, respectively). Thus, we can estimate the statistical average of the physical quantity O as

$$\langle \hat{O} \rangle = {\rm Tr}_{\rm B}(\rho_{\rm B}\hat{O}). \quad (4)$$

Here, the symbol ${\rm tr}_{\rm B}$ indicates the trace over the states of the phonon bath. In particular, if $\hat{O} = b_\lambda^+ b_\lambda$ is the operator of the number of phonons of the λth mode, then we see that the average number of phonons that is conserved over time $\Delta t \sim \tau_{\rm tr}$ is determined by the expression

$$\langle b_\lambda^+ b_\lambda \rangle = n(\omega_\lambda) = [\exp(\hbar\omega_\lambda/k_{\rm B}T) - 1]^{-1}. \quad (5)$$

It coincides with the stationary Bose distribution for the bosons.

2.2. Polaron transform at time-dependent coupling to phonons

Since $\tau_{tr} \to \infty$ for $V_{nn'}(t) \to 0$, based on inequality (2), we can conclude that the absolute value of $V_{nn'}(t)$ is significantly less than the absolute value of $\kappa_n(t)$. Consequently, the electronic states of a dynamic system can participate in the transition process as polaron states. To see the role of these states in the kinetics, we use the transform operation

$$\tilde{H}_{\rm SE}(t) = \hat{R}(t)H_{\rm SE}(t)\hat{R}^{-1}(t) - i\hbar\hat{R}(t)\frac{d}{dt}\hat{R}^{-1}(t), \qquad (6)$$

which was previously used to study adiabatic disturbances [20]. In our case, we propose a unitary transformation matrix in the following form:

$$\hat{R}(t) = \sum_n \hat{S}_n(t)|n\rangle\langle n|, \qquad (7)$$

where

$$\hat{S}_n(t) = \exp\left[\xi_n(t)b^+ - \xi_n(t)b\right] \times$$
$$\times \exp\sum_j(\kappa_j/\hbar\omega_j)(b_j^+ - b_j). \qquad (8)$$

Here, the parameter $\kappa_j = \kappa_{1j}/2 = -\kappa_{2j}/2$ reflects the coupling between the states of the dynamic system and jth mode oscillation mode of the environment. Using Eqs. (7) and (8), we obtain

$$\begin{aligned} &\tilde{H}_{\rm SE}(t) = \tilde{H}_0(t) + H_{\rm int}(t) + H_{\rm B}, \\ &\tilde{H}_0(t) = \textstyle\sum_n \tilde{E}_n(t)|n\rangle\langle n|, \qquad (9) \\ &H_{\rm int}(t) = \textstyle\sum_{n,n'}(1-\delta_{n,n'})\tilde{V}_{nn'}(t)|n\rangle\langle n'|. \end{aligned}$$

where the bath Hamiltonian $H_{\rm B}$ is defined by the Eq. (3). Unlike expression (1), the transformed Hamiltonian (9) includes phonon creation and annihilation operators directly in the "dressed" operator

$$\hat{V}_{nn'}(t) = \hat{S}_n(t)V_{nn'}(t)\hat{S}_{n'}^{-1}(t), \qquad (10)$$

which is responsible for phonon-accompanieding transitions in a dynamic system. Unlike the well-known standard unitary polaron transform, the proposed transform is specified by a time-dependent matrix (8). This dependence is concentrated in the quantities $\xi_n(t)$ satisfying the equation

$$i\frac{d\xi_n(t)}{dt} = \omega_n\xi_n(t) - \kappa_n(t). \qquad (11)$$

This equation follows from the fact that the Hamiltonian (9) does not contain linear terms proportional to the operators b^+ or b.

Based on the solution of Eq. (11), which is

$$\xi_n(t) = \xi_n(0)e^{-i\omega_n t} + (i/\hbar)\int_0^t d\tau\kappa_n(\tau)e^{-i\omega_n(t-\tau)}, \qquad (12)$$

we will be able to specify the time-dependent polaron transformation (8), and, thus, the transition operator (10). Besides, the energy of an open system

$$\tilde{E}_n(t) = E_n(t) + E_r^{(env)} + \Delta E_n(t). \qquad (13)$$

receives an addition in the form of reorganization energy

$$E_r = \sum_j(\kappa_j^2/\hbar\omega_j) \qquad (14)$$

due to the coupling to environmental vibrations, as well as a time-dependent addition

$$\Delta E_n(t) = \hbar\omega_n|\xi_n(t)|^2 - \kappa_n(t)(\xi_n(t) + \xi_n^*(t)) +$$
$$+ \frac{i\hbar}{2}\left[\xi_n(t)\frac{d\xi_n^*(t)}{dt} - \frac{d\xi_n(t)}{dt}\xi_n^*(t)\right]. \qquad (15)$$

2.3. Redfield-type and balance-like kinetic equations for an open system at polaron coupling

Our aim is to obtain kinetic equations for the probability of occupying each nth state of an open system, i.e., values $P_n(t) = {\rm tr}(\rho_{\rm SE}(t)|n\rangle\langle n|)$, where the trace covers all states of the entire $S + E$ system. To this end, we note that relation (6) assumes that the Liouville equation $\dot{\rho}_{\rm SE}(t) = -(i/\hbar)[H_{\rm SE}(t), \rho_{\rm SE}(t)]$ with Hamiltonian (1) transforms into the Liouville equation $\dot{\tilde{\rho}}_{\rm SE}(t) = -(i/\hbar)[\tilde{H}_{\rm SE}(t), \tilde{\rho}_{\rm SE}(t)]$ with Hamiltonian (9), if only the nonequilibrium density operators $\rho_{\rm SE}(t)$ and $\tilde{\rho}_{\rm SE}(t)$ are transformed one into the other using the unitary operator (7), so that $\rho_{\rm SE}(t) = \hat{R}(t)\tilde{\rho}_{\rm SE}(t)\hat{R}^{-1}(t)$. Taking this fact into account and noting that $\hat{R}^{-1}(t)|n\rangle\langle n|\hat{R}(t) = |n\rangle\langle n|$, we see that the occupation probability can be calculated using the expression $P_n(t) = tr(\tilde{\rho}_{\rm SE}(t)|n\rangle\langle n|)$. This value coincides with the diagonal element of the nonequilibrium density matrix $\tilde{\rho}_{\rm SE}(t)$, specified by its elements $\langle n|\tilde{\rho}_{\rm SE}(t)|n'\rangle$.

Using the definition

$$\rho(t) = \mathrm{Tr}_{\mathrm{B}}\tilde{\rho}_{\mathrm{SE}}(t), \tag{16}$$

for the open system density matrix $\rho(t)$, we see that $P_n(t) = \mathrm{tr}_{\mathrm{S}}(\rho(t)|n\rangle\langle n|) = \rho_{nn}(t)$. Here, the trace covers only the states of a dynamic system. The equation for the temporal behavior of $\rho(t)$ follows directly from definition (16) and the Liouville equation for $\tilde{\rho}_{\mathrm{SE}}(t)$ given by the corresponding Hamiltonian Eq. (9). It should be noted that, in this Hamiltonian, the interaction H_{int} plays a role of perturbation. This is due to the polaron effect, in which the "phonon coat" weakens transitions between electronic states of an open quantum system S. Thus, we can use the Born approximation in deviations

$$\Delta\hat{V}_{nn'}(t) = V_{nn'}(t)\big(\hat{S}_n(t)\hat{S}^{-1}_{n'}(t) - \langle\hat{S}_n(t)\hat{S}^{-1}_{n'}(t)\rangle\big), \tag{17}$$

where averaging $\langle ...\rangle$ over bath states is estimated with expression (4). Considering also that, in the Born approximation, the decoupling $\tilde{\rho}_{\mathrm{SE}}(t) \approx \rho(t)\rho_{\mathrm{B}}$ is well satisfied, we come to the following integro-differential equation for the density matrix of an open quantum system, "dressed" by bath phonons:

$$\dot{\rho}(t) = -iL_{\mathrm{S}}(t)\rho(t) - \\ - \int\limits_0^t dt'\mathrm{Tr}_{\mathrm{B}}\big(L_V(t)D(t,t')L_V(t')\rho_{\mathrm{B}}\rho(t')\big), \tag{18}$$

where

$$D(t,t') = \hat{T}\exp{[-i\int\limits_{t'}^t d\tau(L_{\mathrm{S}}(\tau) + L_{\mathrm{B}})]} \tag{19}$$

is the evolution unitary matrix ($\hat{T}$ is the Dayson's time-ordering operator). In Eqs. (18) and (19), $L_{\mathrm{S}}(t) \equiv \hbar^{-1}[H_{\mathrm{S}}(t), ...]$, $L_{\mathrm{B}} \equiv \hbar^{-1}[H_{\mathrm{B}}, ...]$, and $L_V(t) \equiv \hbar^{-1}[\Delta\hat{H_{\mathrm{int}}}(t), ...]$ are the Liouville operators related to the modified Hamiltonian of the quantum system

$$H_{\mathrm{S}}(t) = H_0(t) + \langle H_{\mathrm{int}}(t)\rangle \tag{20}$$

and the modified interaction

$$\Delta H_{\mathrm{int}}(t) = H_{\mathrm{int}}(t) - \langle H_{\mathrm{int}}(t)\rangle\,. \tag{21}$$

In tetradic representation, the master equation (18) looks like a set of Redfield-type kinetic equations for matrix elements $\rho_{nn'}(t) = \langle n|\rho(t)|n'\rangle$. The set reads as

$$\dot{\rho}_{nm}(t) = -\frac{i}{\hbar}(\tilde{E}_n(t) - \tilde{E}_m(t))\,\rho_{nm}(t) - \\ - \frac{i}{\hbar}\sum_l \big(\langle\hat{V}\rangle_{nl}(t)\rho_{lm}(t) - \langle\hat{V}\rangle_{lm}(t)\,\rho_{nl}(t)\big) - \\ - \frac{1}{\hbar^2}\sum_{n'm'}\int\limits_0^t \Gamma_{nm,n'm'}(t,t')\,\rho_{n'm'}(t')\,dt', \tag{22}$$

where the elements of the relaxation supermatrix,

$$\Gamma_{nm,n'm'}(t,t') = \\ = \sum_{rr'}\Big[\big\langle\Delta V_{nr}(t)\Delta V^{\tau}_{r'n'}(t')\big\rangle U_{rr'}(t,t')U^*_{mm'}(t,t') + \\ + \big\langle\Delta V^{\tau}_{m'r'}(t')\Delta V_{rm}(t)\big\rangle U_{nn'}(t,t')U^*_{rr'}(t,t') - \\ - \big\langle\Delta V_{rm}(t)\Delta V^{\tau}_{r'n'}(t')\big\rangle U_{nr'}(t,t')U^*_{rm'}(t,t') - \\ - \big\langle\Delta V^{\tau}_{m'r'}(t')\Delta V_{nr}(t)\big\rangle U_{rn'}(t,t')U^*_{mr'}(t,t')\Big] \tag{23}$$

are determined through correlation functions of the type

$$K_{ab,a'b'}(t,t') = \big\langle\Delta\hat{V}_{ab}(t)\Delta\hat{V}^{\tau}_{a'b'}(t')\big\rangle, \\ K_{ab,a'b'}(t',t) = \big\langle\Delta\hat{V}^{\tau}_{ab}(t')\Delta\hat{V}_{a'b'}(t)\big\rangle, \tag{24}$$

with $\Delta\hat{V}^{\tau}_{ab}(t') = e^{-iH_B\tau/\hbar}\Delta\hat{V}_{ab}(t')e^{iH_B\tau/\hbar}$, where $\tau = t - t'$. Besides, the quantities (23) contain elements $U_{ab}(t,t') = \langle a|U_{\mathrm{S}}(t,t')|b\rangle$ defining a unitary matrix

$$\hat{U}_{\mathrm{S}}(t,t') = \hat{T}\exp\left[-(i/\hbar)\int\limits_{t'}^t H_{\mathrm{S}}(\tau)d\tau\right]. \tag{25}$$

For those open systems, where the average values $\langle\hat{V}_{nn'}(t)\rangle$ disappear and, therefore, $\langle H_{\mathrm{int}}(t)\rangle = 0$, Hamiltonian (20) is diagonal for any t. This reduces the elements $U_{ab}(t,t') = \langle a|\hat{U}_{\mathrm{S}}(t,t')|b\rangle$ of the matrix (25) to a simple form

$$U_{ab}(t,t') = \delta_{a,b}\exp\left[-(i/\hbar)\int\limits_{t'}^t \tilde{E}_a(\tau')d\tau'\right]. \tag{26}$$

If the rotational wave approximation [11] is fulfilled. Then, in the system of equations (22), the mixing of diagonal $\rho_{nn}(t)$ and non-diagonal $\rho_{nm}(t)$ elements of the density matrix becomes insignificant, and we arrive at the following balance-like equations for the probabilities of occupation of the states of a dynamic system:

$$\dot{P}_n(t) = -\frac{1}{\hbar^2}\sum_{n'}\int_0^t \Gamma_{nn,n'n'}(t,t')P_{n'}(t')dt'. \tag{27}$$

3. Results and Discussion

When applying the kinetic equations (23) to the open TLS, we must consider the fact that $n = 1, 2$. Thus, transitions in TLS are associated with the matrix elements $V_{12}(t)$ and $V_{21}(t)$, as well as couplings $\kappa_1(t)$ and $\kappa_2(t)$. We will assume that the matrix elements do not depend on time, and there is no external *ac* field. This means that, in the considered TLS, the time dependence is concentrated only in the couplings $\kappa_n(t)$. Below, based on the spin-boson version of TLS, we set $V_{nn'} = \hbar v$, $\kappa_1(t)/2 = -\kappa_2(t)/2 = \kappa(t)$ and $\omega_1 = \omega_2 = \omega_0$.

3.1. Master equation for TLS under nonstationary coupling with a phonon bath

For simplicity, we assume that the average $\langle \hat{V}_{nn'}(t)\rangle$, Eq. (4) is equal to zero for a certain type of phonon baths [16]. This means that' in the relaxation supermatrix (23), $\Delta\hat{V}_{ab}(t) = \hat{V}_{ab}(t) = \hbar v\hat{S}_a(t)\hat{S}_b^{-1}(t)$. Taking this circumstance into account, we arrive at the balance equations (27) for the occupation probabilities $P_1(t)$ and $P_2(t)$, where quantities $\Gamma_{nn,n'n'}(t,t')$ are determined through the correlation functions $K_{ab,ba}(t,t')$ and $K_{ab,ba}(t',t)$, Eq. (24). In the spin-boson description, the difference in occupation probabilities $\sigma_z(t) = P_1(t) - P_2(t)$ is usually analyzed. With regard for the normalization condition $P_1(t) + P_2(t) = 1$, we arrive at the equation:

$$\dot{\sigma}_z(t) = -\int_0^t g(t,t-\tau)\sigma_z(t-\tau)d\tau - \int_0^t f(t,t-\tau)d\tau, \tag{28}$$

where $g(t,t') = (1/2\hbar^2)(\Gamma_1(t,t') + \Gamma_2(t,t'))$, $f(t,t') = (1/2\hbar^2)(\Gamma_1(t,t') - \Gamma_2(t,t'))$ and

$$\Gamma_n(t,t') = K_{nn',n'n}(t,t')e^{i\omega_{nn'}\tau} + K_{nn',n'n}(t',t)e^{i\omega_{n'n}\tau}. \tag{29}$$

In Eq. (29), the time-independent frequency $\omega_{nn'} = (1/\hbar)(E_n - E_{n'})$ of the $n \to n'$ transition reflects the fact that, in the spin-boson version of TLS, the reorganization energies (14) and time-dependent additions (15) are the same for $n = 1$ and $n = 2$. Therefore, in the absence of the *ac* field according to the Eq. (13) we have $\tilde{E}_n(t) - \tilde{E}_{n'}(t) = E_n - E_{n'}$. Calculation of correlation functions shows that

$$\begin{aligned} &g(t,t-\tau) = \\ &= v^2\big(\Lambda(t,t-\tau) + \Lambda^*(t,t-\tau)\big)\cos\omega_s\tau, \\ &f(t,t-\tau) = \\ &= -iv^2\big(\Lambda(t,t-\tau) - \Lambda^*(t,t-\tau)\big)\sin\omega_s\tau. \end{aligned} \tag{30}$$

Here, $\omega_s = \omega_{12} \geq 0$ is the transition frequency in the open system S and

$$\Lambda(t,t-\tau) = e^{-G_B(\tau)}e^{-G_s(t,t-\tau)} \tag{31}$$

is a factor reflecting the influence of the environment (phonon bath) on transition rates. In Eq. (31), the function

$$G_{\mathrm{B}}(\tau) = \sum_j \alpha_j^2[(2n(\omega_j)+1)(1-\cos\omega_j\tau) + i\sin\omega_j\tau], \tag{32}$$

where $\alpha_j = \kappa_j/\hbar\omega$, is well known in the spin-boson model [12, 16]. As for the function

$$\begin{aligned} &G_s(t,t-\tau) = (1/2)(|\xi(t)|^2 + |\xi(t-\tau)|^2) \times \\ &\times (2n(\omega_0)) + 1) - \big[(n(\omega_0)+1)\xi^*(t)\xi(t-\tau)e^{-\mathrm{i}\omega_0\tau} + \\ &+ n(\omega_0)\xi(t)\xi^*(t-\tau)e^{\mathrm{i}\omega_0\tau}\big], \end{aligned} \tag{33}$$

where $\xi(t) = (-1)^{n+1}\xi_n(t)/2$, it characterizes the influence of the phonon bath on electronic transitions in a quantum system through the non-stationary coupling between the electronic states of the system and internal oscillations of frequency ω_0. Such a transition is accompanied by the creation or annihilation of one or several intramolecular frequencies ω_0, the average number of which is supported by distribution (5) with $\lambda = 0$.

3.2. Example: TLS with a periodic coupling to the Ohmic phonon bath

Analysis of the master equation (28) for occupation probabilities $P_1(t) = (1/2)(1 + \sigma_z(t))$ and $P_2(t) = (1/2)(1 - \sigma_z(t))$ becomes possible, if we specify the type of phonon bath and the function $\kappa = \kappa(t)$. In this paper, we analyze the situation where non-Markovianity is not important, so that $\sigma_z(t-\tau) \approx \approx \sigma_z(t)$ and thus the integro-differential equation reduce to the differential equation

$$\dot{\sigma}_z(t) = -K(t)\sigma_z(t) + F(t), \tag{34}$$

where

$$K(t) = \int_0^t g(t, t-\tau)d\tau \tag{35}$$

can be thought of as the time-dependent transition rate, and

$$F(t) = \int_0^t f(t, t-\tau)d\tau \tag{36}$$

is the time-dependent free term. Note that reducing Eq. (28) to Eq. (34) is carried out with good accuracy, if the Born approximation is used to obtain the relaxation matrix (23). In this case, the manifestation of non-Markovianity occurs in higher orders with respect to matrix elements of type $V_{nn'}$ [2].

To have analytic expressions for the $G_{\mathrm{B}}(\tau)$ in hand, following the spin-boson description [12,15] let us represent this function in the form

$$G_{\mathrm{B}}(\tau) = \frac{1}{2\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \times$$
$$\times\left[(2n(\omega)+1)(1-\cos\omega\tau) + i\sin\omega\tau\right], \tag{37}$$

where $J(\omega) = (2\pi/\hbar^2)\sum_j \kappa_j^2 \delta(\omega - \omega_j)$ is the bath spectral density [13]. Below' we use its Ohmic form [14]

$$J(\omega) = \frac{2\pi E_r}{\hbar\omega_{\mathrm{D}}}\,\omega\theta(\omega_{\mathrm{D}} - \omega), \tag{38}$$

which guarantees the validity of the condition $\langle \hat{V}_{nn'}(t)\rangle = 0$. The Ohmic form depends on the value of the reorganization energy (14) and includes an abrupt cutoff at the Debye frequency ω_{D}.

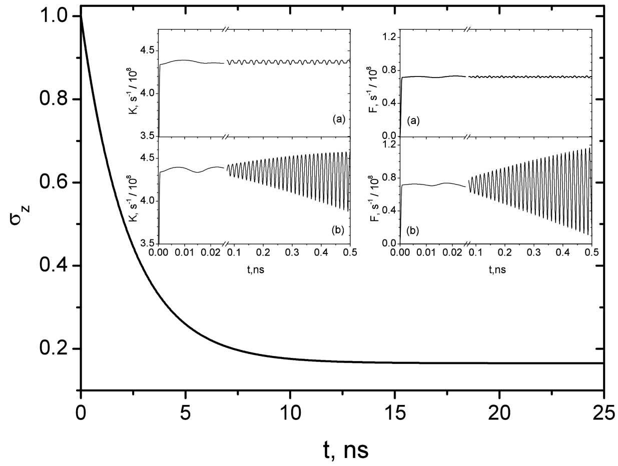

Fig. 1. Temporal behavior of the occupation probabilities of electronic states of an open TLS with periodic changes in the electron-phonon coupling $\kappa(t)$. The insets on the left and right show the time dependences of both the transition rate and the free term of the kinetic equation (34) under conditions of non-resonant (a) and resonant (b) influence of a periodic field on $\kappa(t)$. Three characteristic times of temporal evolution are clearly observed at scales $\Delta t \sim 0.1$ ps, 0.01 ns and 1 ns. Calculations with parameters $T = 300$ K, $E_r = 50$ cm^{-1}, $\hbar\omega_0 = 15$ cm^{-1}, $\hbar\omega_s = 70$ cm^{-1}, $\hbar\omega_D = 5$ cm^{-1}, $\hbar v = 1$ cm^{-1}, $\alpha = 0.25$, $\beta = 0.1$. The resonant regime of 1→2 transitions is estimated at $\omega \simeq \omega_0 = 15$ cm^{-1}

The function $\xi(t) = \xi_1(t) - \xi_2(t)$ is found from the solution of Eq. (5), setting $\kappa_n(t) = \kappa_n + \chi_n(t)$, where κ_n is independent of external influence on the equilibrium position of the nuclei of the system S, and $\chi_n(t)$ is the contribution to the displacement of the equilibrium position due to the external force field. Here, we consider the influence of the periodic field on transitions in S. Assuming $\chi_n(t) = \chi_n \cos\omega t$ and introducing the notations $\alpha = \kappa/\hbar\omega_0$ and $\beta = \chi/\hbar\omega_0$, where $\kappa_1 = -\kappa_2 \equiv \kappa/2$ and $\chi_1 = -\chi_2 \equiv \chi/2$, we get

$$\begin{aligned}
&\xi(t) = \alpha + \beta[\phi_a(t) - i\phi_b(t)],\\
&\phi_a(t) = \frac{1}{1-\zeta^2}(\cos\omega t - \zeta^2\cos\omega_0 t),\\
&\phi_b(t) = \frac{\zeta}{1-\zeta^2}(\sin\omega t - \zeta\sin\omega_0 t), \quad (\zeta \equiv \omega/\omega_0).
\end{aligned} \tag{39}$$

To demonstrate the influence of a periodic field on the time evolution of the populations of the electronic states of the TLS, we will carry out estimates assuming that the TLS is in a nonpolar environment. Figures 1 and 2 show one of the possible scenarios for the development of the TLS kinetics at room temperature in the presence of a non-resonant ($\omega \neq \omega_0$) and resonant ($\omega \simeq \omega_0$) external field, controlling the TLS – environment coupling. In a nonpolar medium, the reorganization energy E_r is in the region of 10–100 cm^{-1}, the energy of the Debye cutoff frequency is about $\hbar\omega_{\mathrm{D}} \sim 10$ cm^{-1}, and the intramolecular op-

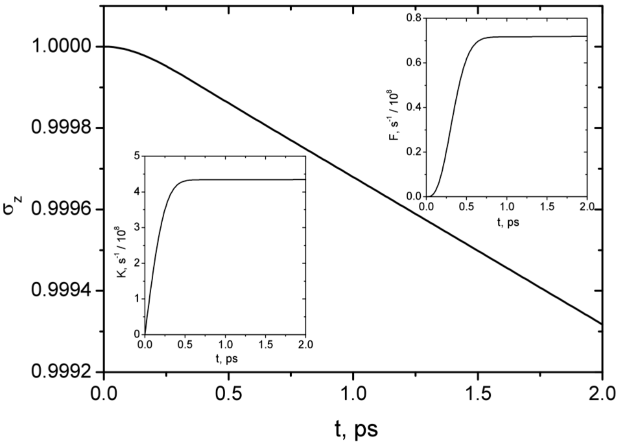

Fig. 2. The initial stage of development of kinetics (scale $\Delta t \sim 0.1$ ps), at which the change in the occupation probabilities of TLS states is insignificant, but the rate $K(t)$ of transition between states increases the evolution time scale to $\Delta t \sim 0.01$ ns)

tical frequency on the order of 10^{-2} eV [14–16]. As for the transition matrix element V_{12}, it can be in a wide range from tenths to hundreds of inverse centimeters. From Fig. 1 it follows that the formation of the transition rate $K(t)$ (and the free term $F(t)$) is due to the time development of three stages of the kinetic process. The fastest one can be estimated by expanding the functions $G_{\rm B}(\tau)$ and $G_{\rm S}(t, t-\tau)$ near $t \simeq 0, \tau = 0$. At room temperature, when $n(\omega_{\rm D}), n(\omega_0) \gg 1$, and, with the use of the Ohmic form of the bath spectral density, we get

$$\begin{aligned} G_{\rm B}(\tau) &\approx i(E_r/\hbar)\tau + (2\omega_{\rm D}k_{\rm B}T/\hbar)\tau^2, \\ G_{\rm S}(t, t-\tau) &\approx (\alpha+\beta)^2[i\omega_0\tau + (2\omega_0 k_{\rm B}T/\hbar)\tau^2]. \end{aligned} \tag{40}$$

Thus, $\tau_{\rm fast}^{-1} \simeq \sqrt{(2k_{\rm B}T/\hbar)[\omega_d + (\alpha+\beta)^2\omega_0]}$. For the values of $\omega_{\rm D}$, ω_0 and T we use, this gives a value of $\tau_{\rm fast} \approx 0.25$ ps, which is in good agreement with the data presented in Fig. 2. The second kinetic stage is fixed on the time scale $\Delta t \sim \omega_0^{-1} \sim 0.02$ ns (Fig. 1). This stage reflects a purely dynamic process that has little effect on the change in the probabilities $P_n(t)$ of occupation of the TLS states. Real changes in the occupation probabilities are associated with the third, slowest stage of the kinetics, which is fixed on the time scale $\Delta t \sim 1$ ns (see Fig. 1). The stage is controlled by the matrix elements $V_{nn'}$, so that the inverse characteristic time of the slowest stage is equal to $\tau_{\rm tr}^{-1} \sim v^2\tau_{\rm fast}$. This gives $\tau_{\rm tr} \sim 1$ ns, which is in good agreement with the time behavior of $\sigma_z = \sigma_z(t)$ shown in Fig. 1.

4. Conclusion

This work shows how a kinetic process is formed in a dynamic system that is in a non-stationary coupling with the environment. It is assumed that the environment has a large number of degrees of freedom, and, therefore, transitions in the dynamic system do not change the state of the environment. However, due to the openness of a dynamic system, the environment is capable of modifying both the states of the system and its energy levels. We are considering a quantum dynamic system, where the exchange of energy between the system and the environment is carried out through vibrational quanta (phonons). Using the method of nonequilibrium statistical mechanics, kinetic equations are obtained that describe the time evolution of the density matrix of a dynamic system under conditions of strong (polaron) coupling with vibrational modes of both the environment and the system. The difference from a similar type of research is that the coupling between the electronic states of the system and its vibration states is assumed to be time-dependent. We have proposed a unitary transformation, which made it possible to account for this non-stationary coupling directly in the operator responsible for transitions between states of the system. This opened up the possibility of using the perturbation method to derive the master equation for the probabilities of occupying system's states. As an example of the application of non-stationary polaron transformation, the kinetics of establishing the probabilities of occupation of electronic states of an open TLS is considered. The influence on the system of an external *ac* field is carried out through a non-stationary coupling of electronic states with the internal oscillation modes of the system and a stationary coupling with the oscillation modes of the environment. Based on the spin-boson version of the TLS, the corresponding kinetic equation for the occupation probabilities is obtained, Eq. (28), as well as the corresponding expressions for the transition rates and the free term. The analysis shows (Fig. 1 and Fig. 2) the presence of three different time scales for the development of the kinetics. One scale of the order of 0.1 ps is due to the stationary interaction of the TLS with the environment, the second scale of the order of 0.01 ns reflects the influence of the non-stationary interaction of electronic and vibronic states inside the TLS, and the third scale of the order of 1 ns is associated with the interaction leading to transitions between the electronic states of the TLS.

Thus, the work shows how the influence of an external *ac* field (in our case, periodic) on the coupling between the electronic and vibrational degrees of freedom of a dynamic system can influence the time development of a kinetic process in an open dynamic system.

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КІНЕТИКА В ДВОРІВНЕВІЙ СИСТЕМІ З СИЛЬНИМ, ЗАЛЕЖНИМ ВІД ЧАСУ ЗВ'ЯЗКОМ ЇЇ СТАНІВ З ФОНОННОЮ ВАННОЮ: СПІН-БОЗОННИЙ ОПИС

За допомогою методів нерівноважної статистичної механіки отримано головне рівняння для матриці густини відкритої дисипативної квантової системи в умовах, коли зв'язок між електронними станами системи та ядерними зміщеннями в ній контролюється змінним полем. Запропоновано залежне від часу перетворення полярону, що дозволило розв'язувати кінетичні рівняння з використанням розкладу за параметром, який характеризує переходи між "одягненими фононами" електронними станами системи. Як приклад показано механізм, який може керувати кінетикою дворівневої системи шляхом прикладання періодичного силового поля до електрон-фононного зв'язку.

Ключові слова: квантова кінетика, дворівнева система, спін-бозонна модель.