Based on the non-equilibrium density matrix method and using the Bogolyubov’s approach for the decoupling of many-particle distribution functions, a closed set of kinetic equations is derived for the state occupancies of closed and open quantum systems. It is shown that the transformation of a non-Markovian master equation into a Markovian one becomes possible at a high-frequency stochastic field alternating the energy levels of a quantum system. At a weak interaction between quantum subsystems composing the open quantum system, the set of linear balance-like kinetic equations for multistate occupancies of the system is transformed into a set of nonlinear kinetic equations for the occupancies of separate quantum subsystems.

1. Introduction

The most general way to derive a master equation for the state occupancies of closed and open quantum systems (CQS and OQS, respectively) is based on two approaches. The first one utilizes the method of projection operators [1–3]. The second approach employs the Bogolyubov’s method of asymptotic description of the evolution of dynamic systems (the principle of correlation weakening) [4–6]. Both approaches lead to identical kinetic equations for the OQS. In what follows, we employ the projection operators method which has been earlier used to derive the kinetic equations for the description of the charge transmission through single molecules and molecular wires [7–9]. The present generalization takes a possible control of transfer processes by external high-frequency stochastic fields into consideration. The main aim of the present communication is to derive master equations suitable for the description of kinetic processes in closed and open quantum systems composed of separate subsystems. The subsystems are assumed to be coupled to one another and to an equilibrium environment via off-diagonal interactions.

2. Master Equation for the Closed Quantum System

The closed quantum system is a dynamic system, where transitions between its states are determined by only interactions within the system, whereas both the system-environment energy exchange and the particle exchange are ignored. Let \( |a\rangle \) and \( E_a \) be, respectively, the proper state and the proper energy of the CQS Hamiltonian \( H_0 \). This Hamiltonian has to include the main interactions in the CQS. Transitions between the \( a \)th and the \( b \)th states are associated with the off-diagonal transfer operator \( V \).

To generalize a situation, we suppose that the position of CQS energy levels can be alternated by regular ac-fields or non-regular stochastic fields so that the energy of the \( a \)th state becomes \( E_a(t) = E_a + \Delta E_a(t) \). In the basis of proper states \( \{ |a\rangle \} \), a total CQS Hamiltonian appears as

\[
H_{\text{CQS}}(t) = H + \Delta H(t),
\]

where

\[
H = H_0 + V
\]

is the basic CQS Hamiltonian, with

\[
H_0 = \sum_a E_a |a\rangle \langle a|
\]

and

\[
V = \sum_{a,b} V_{ab} (1 - \delta_{a,b}) |a\rangle \langle b|
\]

being its diagonal and off-diagonal parts, respectively. In the model under consideration, the influence of an external ac-field is completely concentrated in the state energy via the addition

\[
\Delta H(t) = \sum_a \Delta E_a(t) |a\rangle \langle a|
\]

where \( \Delta E_a(t) \) is the energy variation caused by regular or/and stochastic fields.
The derivation of a master equation describing the evolution of state occupancies starts from the Liouville equation for the CQS’s density matrix \( \rho_{CQS}(t) \):

\[
\dot{\rho}_{CQS}(t) = -i\mathcal{L}(t)\rho_{CQS}(t) .
\]  

(6)

Here, \( \mathcal{L}(t) = (1/\hbar)[H_{CQS}(t), \ldots] \) is the Liouville superoperator associated with Hamiltonian (1). In line with the basic master equation (8), one arrives to an evolution operator reads \( S(t, t - \tau) = S_0(t, t - \tau) = \exp[-i\int_{t - \tau}^{t}d\tau'\mathcal{L}_0(\tau')] \), and, thus, elements (11) of the transfer matrix \( \mathcal{G}(t, t - \tau) \) appear in a simple form

\[
\mathcal{G}_{ab}(t, t - \tau) = (2/\hbar^2)|V_{ba}|^2 \cos[\omega_{ba}\tau + \Phi_{ba}(t, t - \tau)] ,
\]  

(11)

define the transfer matrix \( \mathcal{G}(t, t - \tau) \). Master equation (10) is exact and can be used for a further reduction to the master equation for state occupancies. Before, however, we show how master equation (10) is transformed into a set of kinetic equations, where the transitions are specified by the only rate constants. To this end, let us consider the Born approximation, where an evolution operator reads \( \mathcal{S}(t, t - \tau) = S_0(t, t - \tau) = \exp[-i\int_{t - \tau}^{t}d\tau'\mathcal{L}_0(\tau')] \), and, thus, elements (11) of the transfer matrix \( \mathcal{G}(t, t - \tau) \) appear in a simple form

\[
\mathcal{G}_{ab}(t, t - \tau) = (2/\hbar^2)|V_{ba}|^2 \cos[\omega_{ba}\tau + \Phi_{ba}(t, t - \tau)],
\]  

(12)

where

\[
\omega_{ba} = (E_b - E_a)/\hbar
\]  

(13)

is the stationary transition frequency between the \( a \)th and the \( b \)th states, while

\[
\Phi_{ba}(t, t - \tau) = \Phi_b(t, t - \tau) - \Phi_a(t, t - \tau)
\]  

(14)

is the phase difference caused by external ac-fields. Note that, for the \( a \)th state, this time-dependent phase is defined by the expression

\[
\Phi_a(t, t - \tau) = \frac{1}{\hbar} \int_{t - \tau}^{t}d\tau'\Delta E_a(\tau').
\]  

(15)

Here, the quantities

\[
\mathcal{G}_{ab}(t, t - \tau) = -\langle a|(\mathcal{L}_V S(t, t - \tau) \mathcal{L}_V |b\rangle\langle b)|a\rangle
\]  

(11)

define the transfer matrix \( \mathcal{G}(t, t - \tau) \). Master equation (10) is exact and can be used for a further reduction to the master equation for state occupancies. Before, however, we show how master equation (10) is transformed into a set of kinetic equations, where the transitions are specified by the only rate constants. To this end, let us consider the Born approximation, where an evolution operator reads

\[
\mathcal{S}(t, t - \tau) = S_0(t, t - \tau) = \exp[-i\int_{t - \tau}^{t}d\tau'\mathcal{L}_0(\tau')],
\]  

and, thus, elements (11) of the transfer matrix \( \mathcal{G}(t, t - \tau) \) appear in a simple form

\[
\mathcal{G}_{ab}(t, t - \tau) = (2/\hbar^2)|V_{ba}|^2 \cos[\omega_{ba}\tau + \Phi_{ba}(t, t - \tau)],
\]  

(12)

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\[
\omega_{ba} = (E_b - E_a)/\hbar
\]  

(13)

is the stationary transition frequency between the \( a \)th and the \( b \)th states, while

\[
\Phi_{ba}(t, t - \tau) = \Phi_b(t, t - \tau) - \Phi_a(t, t - \tau)
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(14)

is the phase difference caused by external ac-fields. Note that, for the \( a \)th state, this time-dependent phase is defined by the expression

\[
\Phi_a(t, t - \tau) = \frac{1}{\hbar} \int_{t - \tau}^{t}d\tau'\Delta E_a(\tau').
\]  

(15)

If the ac-field is regular, the phase \( \Phi_a(t, t - \tau) \) is a regular function. Therefore, the action of a regular ac-field does not bring to relaxation (damping) transitions in the CQS. A basically another situation is formed if the CQS is under influence of a stochastic field. In this case, the \( \Delta E_a(\tau)/\hbar \equiv \alpha(\tau) \) is a random value, and, thus, the phase \( \Phi_a(t, t - \tau) \) becomes a random functional. As a result, the master equation (10) appears as a stochastic equation. For the description of specific transfer processes, this stochastic equation has to be averaged with respect to a realization of the random quantity \( \alpha(\tau) \). The examples of such an averaging can be found, for instance, in [11–15]. The main result of the averaging is that one obtains the set of coupled equations including not only an equation for averaged state occupancies \( P(a; t) = \langle \langle P(a; t) \rangle \rangle \), but for additional averaged values as well. However, for
the fast random realizations of $\alpha(\tau)$ in comparison with the transfer process within the quantum system, the decoupling procedure $\langle [G_{ab}(t,t-\tau)P(a(t),t-\tau)\rangle \approx \langle [\bar{G}(t,t-\tau)\rangle]P(a(t),t-\tau)$ is valid with a high accuracy. A very important result is that, independently on the type of a stochastic process, the averaged transfer matrix, $\langle [\bar{G}(t,t-\tau)\rangle]$, loses its dependence on the current time $t$ and obtains the damping factors like $\exp (-\gamma_\tau t)$ with $\gamma_\tau > 0$. For instance, in the simplest case of a symmetric dichotomous process ($\alpha(\tau) = \pm \sigma$), the averaging yields $\langle [\bar{G}_{ab}(t,t-\tau)\rangle] = \exp (-\gamma_\tau)Q_{ab}(\tau)$, where $\gamma = \sigma^2/4\nu$ ($\nu$ and $\sigma$ are, respectively, the characteristic frequency and the amplitude of the random process). Consequently, the averaged master equation reads

$$\dot{P}(a;t) = -\sum_{b(\neq a)} \int_0^\tau d\tau e^{-\gamma_\tau t}Q_{ab}(\tau)[P(a;t-\tau) - P(b;t-\tau)], \quad (16)$$

where $\tau_0 = \gamma^{-1}$ is the decay parameter, and $Q_{ab}(\tau)$ is the regular part of the kernel. It follows from integro-differential equation (16) that the characteristic time of the kernel decrease, $\tau_d$, is associated with a stochastic influence, while the characteristic time of the transfer process, $\tau_{tr}$, is determined by an off-diagonal interaction within the CQS (i.e., by matrix elements $V_{ba}$). Note that $P(a;t-\tau) = \exp (-\gamma_d t/\pi)P(a;t)$. In the case of fast stochastic processes under consideration, the strong inequality $\tau_d \ll \tau_{tr}$ is satisfied. Therefore, on the time scale of the transfer process, $\Delta t \sim \tau_{tr}$, the factor $\exp (-\gamma_d t/\pi)$ can be estimated as $\exp (-\tau_d/\tau_{tr}) \approx 1$. This means that, with a high accuracy, one can set $P(a;t-\tau) \approx P(a;t)$, by ignoring, thus, a role of memory processes in the formation of transitions between the CQS states. In view of this fact, one can perform the complete integration with respect to $\tau$. Setting $\exp (-\tau_d/\tau_{tr}) \approx 0$, we obtain, thus, the following Markov’s version of a master equation for the averaged occupancies:

$$\dot{P}(a;t) = -\sum_{b(\neq a)} K(a,b)[P(a;t) - P(b;t)]. \quad (17)$$

Here, the quantity $K(a,b) = (2/\hbar^2)|V_{ba}|^2[\gamma/(\omega_{ba}^2 + \gamma^2)]$ exhibits itself as the rate constant characterizing the interstate transitions. The parameter $\gamma$ could be treated as the broadening of energy levels caused by a stochastic field. If the stochastic field has a complicated form, a simple expression for the $K_{ab}$ is not more valid. But, independently of the precise form of stochastic influence, the main physical result remains correct. Namely, the fast alternation of the stochastic field leads to the transformation of the non-Markovian master equation into a Markovian one. Note now that the area covered by the Lorentzian $\gamma/(\omega^2 + \gamma^2)$ in the region $-\infty < \omega < +\infty$, is independent of the parameter $\gamma$. Therefore, it becomes possible to simplify the form of the rate constant, by setting $\gamma \approx 0$. With regard for the relation $\lim_{\omega \to 0}(1/\pi)\gamma/(\omega^2 + \gamma^2) = \delta(\omega)$, this yields $K(a,b) = (2\pi/\hbar)|V_{ba}|^2\delta(E_b - E_a)$. The advantage is that the rate constant can be calculated now without specification of stochastic fields acting on the CQS. But, one can remember that, physically, the appearance of rate constants describing the transitions in the CQS becomes possible at a strong dephasing caused by the fast alternating stochastic field. If the Born approximation is not used, one derives the following generalized expression for a rate constant:

$$K(a,b) = \frac{2\pi}{\hbar}|V_{ba}^{(tr)}|^2\delta(E_b - E_a). \quad (18)$$

In Eq. (18), $V_{ba}^{(tr)} = \langle b|V^{(tr)}|a \rangle$ is the transition matrix element on the energy surface $E = E_a = E_b$. It is calculated with the transition operator

$$V^{(tr)} = V + VG(E)V, \quad (19)$$

where $G(E) = (E - H + i0^+)^{-1}$ is the Green’s operator, with $H$ being the CQS Hamiltonian (5). Note that form (19) is employed widely for the description of scattering processes, when the initial, $|a \rangle$, and the final, $|b \rangle$, states belong to the colliding particles with and without changes in their compositions [16]. Thus, in the scattering theory, each $a$th state includes, with necessity, the states of continuous spectrum of the particle. Our derivation of master equation (17) shows that the interstate transitions in a CQS can be described by a closed set of kinetic equations (17) for the averaged state occupancies $P(a;t)$ if only the CQS energy levels are casually shifted by a fast stochastic field. In this case, the transitions between CQS states are characterized by the averaged rate constants (18), even though the CQS does not contain a continuous spectrum. In fact, the continuous spectrum is imitated by the fast stochastic field.

3. Master Equation for a Dynamic Subsystem

Let $\Lambda_s$ be the $s(=1,2,...)$th dynamic subsystem of the entire CQS. Subsystem $\Lambda_s$ is associated either with a precise CQS unit (for instance, with electrodes or a molecule) or/and with different degrees of freedom (electronic, nuclear, spin). Denoting, by $j_s(\Lambda_s)$, a specific
quantum state related to the \( \Lambda_s \)th subsystem, one can represent a proper state of Hamiltonian (3) as a set \( \{ j(\Lambda) \} \) of possible quantum states of the CQS. Therefore, master equation (17) reads

\[
\dot{P}(\{ j(\Lambda) \}); t) = - \sum_{\{ j'(\Lambda') \}} K(\{ j'(\Lambda') \}, \{ j(\Lambda) \}) \times
\times [P(\{ j(\Lambda) \}); t) - P(\{ j'(\Lambda') \}); t)].
\]

(20)

[Subsystem \( \Lambda'_s \) can differ from the \( \Lambda_s \) by another charge or/and conformation, as well as by a spin state.] Note the validity of a normalization condition

\[
\sum_{\{ j(\Lambda) \}} P(\{ j(\Lambda) \}); t) = 1.
\]

(21)

The precise form for the rate constant

\[
K(\{ j'(\Lambda') \}, \{ j(\Lambda) \}) = \frac{2\pi}{\hbar} \left( \sum_{\{ j'(\Lambda') \} |(\{ j'(\Lambda') \}|V^{(tr)}|\{ j(\Lambda) \})(j(\Lambda))|^2 \times
\times \delta[E(\{ j'(\Lambda') \}) - E(\{ j(\Lambda) \})] \right)
\]

(22)

depends strongly on the structure of the matrix element

\[
\langle \{ j'(\Lambda') \}|V^{(tr)}|\{ j(\Lambda) \} \rangle = \langle \{ j'(\Lambda') \}|V|\{ j(\Lambda) \} + \sum_{\{ j(\Lambda) \}} \sum_{\{ j'(\Lambda') \}} \langle \{ j'(\Lambda') \}|V|\{ j'(\Lambda') \} \times
\times \langle \{ j'(\Lambda') \}|G(E)|\{ j(\Lambda) \} \rangle \langle \{ j'(\Lambda') \}|V|\{ j(\Lambda) \} \rangle \right)
\]

(23)

characterizing the transitions between the CQS states. To estimate this matrix element, let us note that any CQS state can be represented generally as \( |\alpha \rangle \equiv |\{ j(\Lambda) \} \rangle = \sum_{j_1,j_2,...} C_{j_1(\Lambda_1),j_2(\Lambda_2),...,j_r(\Lambda_r)} |j_1(\Lambda_1),j_2(\Lambda_2),...,j_r(\Lambda_r) \rangle \). Below, for the sake of simplicity, we consider only the form \( |\{ j(\Lambda) \} \rangle = |j_1(\Lambda_1),j_2(\Lambda_2),j_3(\Lambda_3),...,j_r(\Lambda_r) \rangle \) valid in the case of a negligible exchange interaction between the CQS subsystems. Let \( V^{(tr)} \) couple the states belonging to a limited number of subsystems, say, \( \Lambda_1, \Lambda_2,..., \Lambda_r \). Then

\[
\langle \{ j'(\Lambda') \}|V^{(tr)}|\{ j(\Lambda) \} \rangle = \prod_{l \neq 1,...,r} \delta_{j_l(\Lambda_l),j_l(\Lambda'_l)} \times
\times \langle j'_1(\Lambda'_1),...,j'_r(\Lambda'_r)|V^{(tr)}|j_1(\Lambda_1),...,j_r(\Lambda_r) \rangle.
\]

(24)

Form (24) shows that one can sum both parts of Eq. (20) over the states \( j_{l+1}(\Lambda_{l+1}),j_{l+2}(\Lambda_{l+2}),...,j_r(\Lambda_r) \) which are not involved in the transition \( j'_1(\Lambda'_1),...,j'_r(\Lambda'_r) \leftrightarrow j_1(\Lambda_1),...,j_r(\Lambda_r) \). Such a summation brings about the master equation

\[
\dot{P}(j_1(\Lambda_1),...,j_r(\Lambda_r); t) =
\]

\[
= - \sum_{\{ j(\Lambda) \}} \sum_{\{ j'(\Lambda') \}} K(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r); j_1(\Lambda_1),...,j_r(\Lambda_r)) \times
\times [P(j_1(\Lambda_1),...,j_r(\Lambda_r); t) - P(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r); t)]
\]

(25)

for the partial multistate occupancies

\[
P(j_1(\Lambda_1),...,j_r(\Lambda_r); t) = \sum_{\{ j(\Lambda) \}} P(\{ j(\Lambda) \}); t)
\]

(26)

which, in line with Eq. (21), satisfy the normalization condition

\[
\sum_{\{ j(\Lambda) \}} P(\{ j_1(\Lambda_1),...,j_r(\Lambda_r) \}); t) = 1.
\]

(27)

In Eq. (25), the rate constants are determined as

\[
K(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r); j_1(\Lambda_1),...,j_r(\Lambda_r)) =
\]

\[
= \frac{2\pi}{\hbar} \left( |j'_1(\Lambda'_1),...,j'_r(\Lambda'_r)|V^{(tr)}|j_1(\Lambda_1),...,j_r(\Lambda_r) \rangle|^2 \times
\times \delta[E(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r)) - E(j_1(\Lambda_1),...,j_r(\Lambda_r))] \right).
\]

(28)

The set of linear equations (25) can be used to get a kinetic equation for state occupancies \( P(j_s(\Lambda_s); t) \) of a separate subsystem \( \Lambda_s \). Summing Eq. (25) over all states \( j_1(\Lambda_1),...,j_r(\Lambda_r) \) except \( j_s(\Lambda_s) \), one derives

\[
\dot{P}(j_s(\Lambda_s); t) =
\]

\[
= - \sum_{\{ j(\Lambda) \} \neq j_s(\Lambda_s)} \sum_{\{ j'(\Lambda') \}} K(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r); j_1(\Lambda_1),...,j_r(\Lambda_r)) \times
\times [P(j_1(\Lambda_1),...,j_r(\Lambda_r); t) - P(j'_1(\Lambda'_1),...,j'_r(\Lambda'_r); t)],
\]

(29)

where the subsystem state occupancy is normalized by the condition

\[
\sum_{j_s(\Lambda_s)} P(j_s(\Lambda_s); t) = 1.
\]

(30)
4. Master Equation for an Open Quantum System

The above-derived kinetic equations describe the evolution behavior of a dynamic system isolated from the environment. For such systems, the forward and the backward rate constants coincide completely (see the right-hand side of the basic master equation (20) and its particular cases, Eqs. (25) and (29). As a result, at \( t \gg \tau_{tr} \) (\( \tau_{tr} \) is the characteristic time of evolution processes in the CQS), the identical steady occupancies are established for all CQS states \( \{ j(\Lambda) \} \) participating in the transition process. The situation is strongly changed for an OQS.

4.1. Kinetic equation for partial occupancies

To derive a master equation for the OQS, let consider the CQS which is in a contact with the environment. The environment can be considered as a specific subsystem \( \Lambda_e \) of the combined system "CQS + environment". We again come to the master equation (20), but the evolution of state occupancies is determined now not only by the transitions between subsystems (or within a separate subsystem) but is controlled by the environment. This fact is reflected in master equation (25), where, along with the above-indicated states \( j_1(\Lambda_1), \ldots, j_r(\Lambda_r) \) and \( j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}) \), the sets of environmental states, \( j_e(\Lambda_e) \) and \( j'_e(\Lambda'_e) \), are also included in the common state. Therefore, instead of the occupancies \( P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) \) and \( P(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}); t) \), the more complicated occupancies \( P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r), j_e(\Lambda_e); t) \) and \( P(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}), j'_e(\Lambda'_e); t) \) are involved into the transition process. At the same time, the rate

\[
K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'})) = K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}))
\]

An important property of the environment is that the evolution behavior of its state occupancies \( P(\{ j_e(\Lambda_e) \}; t) \) is not practically affected by a dynamic system but is determined by a much stronger interaction with the outside surrounding. This circumstance allows us to employ the Bogolyubov-type decoupling procedure \( P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r), j_e(\Lambda_e); t) \approx P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t)P(j_e(\Lambda_e); t) \). Such a decoupling assumes also that \( E(j_1(\Lambda_1), \ldots, j_r(\Lambda_r), j_e(\Lambda_e)) \approx E(j_1(\Lambda_1), \ldots, j_r(\Lambda_r)) + E(j_e(\Lambda_e)) \). Another important property is that the characteristic time \( \tau_e \) of the establishment of environmental steady-state occupancies is much less than those for the subsystems, i.e. \( \tau_e \ll \tau_{tr} \). Since the evolution of the occupancies of subsystems occurs on a time scale \( \Delta t \gg \tau_e \), we can set \( P(j_e(\Lambda_e); t \gg \tau_e) \approx W(j_e(\Lambda_e)) \) and \( P(j'_e(\Lambda'_e); t \gg \tau_e) \approx W(j'_e(\Lambda'_e)) \) on a time scale \( \Delta t \sim \tau_{tr} \), where \( W(j_e(\Lambda_e)) \) and \( W(j'_e(\Lambda'_e)) \) are the equilibrium environmental steady-state occupancies. When the environment is in a thermal contact with an outside surrounding, this environment appears as a thermal bath with the bath distribution function

\[
W(j_e(\Lambda_e)) = \frac{1}{Z(\Lambda_e)} e^{-E(j_e(\Lambda_e))/k_B T},
\]

where \( Z(\Lambda_e) = \sum_{j_e(\Lambda_e)} e^{-E(j_e(\Lambda_e))/k_B T} \) is the partition sum (\( k_B \) and \( T \) are the Boltzmann’s constant and the absolute temperature, respectively). In condensed matter, the environmental states are often associated with vibration states of nuclei. In this case, each environmental state \( j_e \) coincides with the number of vibration quanta \( n_{\lambda} = 0, 1, 2, \ldots \) of the \( \lambda \)-th mode of the frequency \( \omega_{\lambda} \), while \( E(j_e(\Lambda_e)) = \sum_{\lambda} h \omega_{\lambda} (n_{\lambda} + 1/2) \).

By taking the decoupling procedure into account and by using the normalization condition \( \sum_{j_e(\Lambda_e)} W(j_e(\Lambda_e)) = 1 \), we reduce master equation (25) to the form

\[
\dot{P}(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) =
- \sum_{\{ j_e(\Lambda_e) \} \neq \{ j(\Lambda) \}} \left[ K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'})) \times P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) - P(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}); t) \right] \times \times P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) 
- K(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}); j_1(\Lambda_1), \ldots, j_r(\Lambda_r)) \times \times P(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}); t)
\]

Here, the forward rate constant reads

\[
K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'})) =
\sum_{j_e(\Lambda_e)} \sum_{j'_e(\Lambda'_e)} W(j_e(\Lambda_e)) \times \times K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r), j_e(\Lambda_e); j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}))
\]

where

\[
K(j'_1(\Lambda'_1), \ldots, j'_{r'}(\Lambda'_{r'}), j_e(\Lambda_e); j_1(\Lambda_1), \ldots, j_r(\Lambda_r), j'_e(\Lambda'_e)) =
\]
K\text{stants are connected by the relation Eqs. (34) and (31), the backward and forward rate con-
jugated to the equilibrium environment. The expression for the backward rate constant follows from Eq. (33) if one substitutes the environmental steady occupancy $W(j_r(\Lambda_r))$ for $W(j'_r(\Lambda'_r))$. Note that, in line with Eqs. (34) and (31), the backward and forward rate constants are connected by the relation

$$K(j'_r(\Lambda'_r), j'_r(\Lambda'_r) \rightarrow j_1(\Lambda_1), \ldots, j_r(\Lambda_r)) \times$$

$$\times \exp \left[ -\frac{E(j'_r(\Lambda'_r), \ldots, j_r(\Lambda_r))}{k_B T} \right] =$$

$$= K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r) \rightarrow j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r)) \times$$

$$\times \exp \left[ -\frac{E(j_1(\Lambda_1), \ldots, j_r(\Lambda_r))}{k_B T} \right].$$

The equation for the occupancy of a separate subsystem follows directly from Eq. (32) and reads

$$\dot{p}(j_s(\Lambda_s); t) =$$

$$= \sum_{\{j_1(\Lambda_1)\} \neq \{j_s(\Lambda_s)\}} \sum_{\{j'_1(\Lambda'_1)\}} \left[ K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r) \rightarrow$$

$$\rightarrow j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r)) P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) -$$

$$- K(j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r) \rightarrow j_1(\Lambda_1), \ldots, j_r(\Lambda_r)) \times$$

$$\times P(j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r); t) \right].$$

Here, the rate constants are given by expressions (33)–(35).

### 4.2. Nonlinear master equation

Let the interaction between the subsystems be so weak that Hamiltonian (3) contains no interactions that mix the states related to different subsystems. So, the coupling between the subsystems is completely associated with the weak off-diagonal interaction (4). This allows us to represent a common quantum state as a direct product of partial states $|j_1(\Lambda_1)\rangle$,

$$|\{j(\Lambda)\}\rangle = |j_1(\Lambda_1)\rangle \times |j_2(\Lambda_2)\rangle \times \cdots = \prod_{l} |j_1(\Lambda(l))\rangle.$$

Analogously, the proper energy $E(\{j(\Lambda)\})$ appears as the sum of partial energies $E(j_1(\Lambda_1))$ related to separated subsystems,

$$E(\{j(\Lambda)\}) = E(j_1(\Lambda_1)) + E(j_2(\Lambda_2)) + \cdots$$

$$= \sum_k E(j_k(\Lambda_k)).$$

Since the proper state (37) is the product of separate $\Lambda_1$-th states, one can utilize the ansatz, where a multistate occupancy is represented as the product of partial occupancies (see also refs. [7, 8]), i.e.

$$P(j_1(\Lambda_1), j_2(\Lambda_2), \ldots; t) = \prod_{l} P(j_l(\Lambda_l); t).$$

Here, each partial occupancy satisfies the normalization condition (30).

With the use of ansatz (39), Eq. (36) is transformed into a nonlinear master equation for partial occupancies,

$$\dot{p}(j_s(\Lambda_s); t) =$$

$$= - \sum_{\{j(\Lambda)\} \neq \{j_s(\Lambda_s)\}} \sum_{\{j'_1(\Lambda'_1)\}} \left[ K(j_1(\Lambda_1), \ldots, j_r(\Lambda_r) \rightarrow$$

$$\rightarrow j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r)) P(j_1(\Lambda_1), \ldots, j_r(\Lambda_r); t) -$$

$$- K(j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r) \rightarrow j_1(\Lambda_1), \ldots, j_r(\Lambda_r)) \times$$

$$\times P(j'_1(\Lambda'_1), \ldots, j'_r(\Lambda'_r); t) \right].$$

Here, the rate constants are given by expressions (33)–(35).
Here, the rate constant is given by Eq. (33), where \( E(j_1'\Lambda_1), \ldots, j_r'\Lambda_r) \) \( \simeq \sum_{i=1}^n E(j_i'\Lambda_i) \) and \( E(j_1\Lambda_1), \ldots, j_r\Lambda_r) \) \( \simeq \sum_{i=1}^n E(j_i\Lambda_i) \).

The nonlinear master equation (36) reduces to a simple form, when only two subsystems, \( \Lambda_s \) and \( \Lambda_r \), are involved in a transition process. Thus, the equation for the occupancy of the \( j_s(\Lambda_s) \) state appears as

\[
\dot{P}(j_s(\Lambda_s); t) = -\sum_{j'_s(\Lambda'_s) \neq j_s(\Lambda_s)} \sum_{j'_r(\Lambda'_r)} \sum_{j'_r(\Lambda'_r)} \left[ K(j_s(\Lambda_s), j'_r(\Lambda_r) \rightarrow j'_s(\Lambda'_s), j'_r(\Lambda'_r)) \right]
\]

\[
- \sum_{j'_s(\Lambda'_s)} \sum_{j'_r(\Lambda'_r)} \left[ K(j'_s(\Lambda'_s), j'_r(\Lambda'_r) \rightarrow j_s(\Lambda_s), j_r(\Lambda_r)) \right] \times
\]

\[
\times |(j'_s(\Lambda'_s), j'_r(\Lambda'_r))| V(\Lambda_s, \Lambda_r)|j_s(\Lambda_s), j_r(\Lambda_r)\rangle |j'_s(\Lambda'_s), j'_r(\Lambda'_r)\rangle|^2 \times
\]

\[
\times \delta [E(j'_s(\Lambda'_s)) + E(j'_r(\Lambda'_r)) + E(j_s(\Lambda_s)) - E(j_s(\Lambda_s))]
\]

\[
- [E(j_s(\Lambda_s)) + E(j_r(\Lambda_r)) + E(j_s(\Lambda_s))]
\]

(41)

is the rate constant characterizing the transition between two subsystems.

The simplest form of a kinetic equation is established to describe the evolution within a separate subsystem. Actually, if the \( j_s(\Lambda_s) \rightarrow j'_s(\Lambda'_s) \) transitions are accomplished without participation of any additional subsystem, the nonlinear master equation (41) reduces to a linear one,

\[
\dot{P}(j_s(\Lambda_s); t) = -\sum_{j'_s(\Lambda'_s)} [K(j_s(\Lambda_s) \rightarrow j'_s(\Lambda'_s)) P(j_s(\Lambda_s); t) - K(j'_s(\Lambda'_s) \rightarrow j_s(\Lambda_s)) P(j'_s(\Lambda'_s); t)]
\]

(43)

The expression for the backward rate constant follows from Eq. (44) if one substitutes \( W(\{j_s(\Lambda_s)\}) \) for \( W(\{j'_s(\Lambda'_s)\}) \). Note that, due to a direct coupling of the subsystem to the environment, the transitions within the subsystem are mainly performed with the first term in the effective transfer operator (19).

5. Conclusion

In the given communication, the rigorous derivation of different types of master equations is carried out for state occupancies belonging to the both closed and open quantum systems. The derivation starts from an exact Liouville equation for the density matrix of a quantum system affected by a high-frequency stochastic field. Just owing to the stochastic field, the master equation for the diagonal density matrix is transformed into a Markov-type operator equation reducing thus the master equation for occupancies into linear balance-like kinetic equations with respective rate constants. Generally, these rate constants characterize transitions between the CQS states, Eq. (20), as well as the evolution of partial occupancies, Eq. (25). When the CQS contacts with an equilibrium environment, it is transformed to an OQS. Now, the master equation for multistate partial occupancies and the master equation for the state occupancy of a separate quantum subsystem are given by Eqs. (36) and (40), respectively. All noted equations are linear ones. But, in the case of a weak interaction between quantum subsystems, the noted sets of balance-like equations are transformed into a set of nonlinear kinetic equations for single-state occupancies, Eq. (40). Note that such a transformation is strictly correct if only one employs the Born approximation for operator (19).

The main criterion employed to derive the master equation for multistate occupancies of a CQS is that the characteristic time of the damping process caused by the alteration of a stochastic field, \( \tau_d \), and the characteristic time of transition processes in the CQS, \( \tau_{tr} \), satisfy the condition \( \tau_{tr} \gg \tau_d \). In the case of an OQS, this criterion reads as \( \tau_{tr} \gg \tau_c \gg \tau_d \), where \( \tau_c \) is the characteristic time of the establishment of a thermal equilibrium in the environment (thermal bath). For instance, in molecular systems, the stochastic fields can be created by small alteration of valent bonds (frequencies of the order \( 10^{13} \text{s}^{-1} \)). This yields \( \tau_c \sim (10^{-12} - 10^{-13}) \text{s} \). As to the characteristic time for the vibration relaxation associated with \( \tau_c \), it varies in a wide interval.
Therefore, the above conditions for the derivation of master equations are satisfied.

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КЕРУЮЧЕ РІВНЯННЯ ДЛЯ ЗАСЕЛЕНОСТЕЙ СТАНІВ ВІДКРИТОЇ КІВАНТОВОЇ СИСТЕМИ

Е.Г. Петров

Грунтуючись на методі нерівноважної матриці густини та використовуючи метод Боголюбова для розщеплення багаточастинкової функції розподілу, отримано замкнуту систему кінетичних рівнянь для заселеності станів як замкнutoї, так і відкритої квантовах систем. Показано, що трансформація немарковського керуючого рівняння в марковське стає можливою при високочастотному стохастичному полi, яке зсуває енергетичні рівні квантової системи. При слабкій взаємодії між квантовими підсистемами, що складають цілу квантову систему, система лінійних балансних кінетичних рівнянь для заселеності багаточастинкових станів переходить у систему нелінійних кінетичних рівнянь для заселеності окремої квантової підсистеми.