MARKOV FORM OF THE METHOD OF nonequilibrium statistical operator

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Abstract

The general principles of the choice of the reduced description parameters of nonequilibrium states $\gamma_\alpha(t)$ and the construction of the nonequilibrium statistical operator (NSO) $\rho(t)$ are discussed. On the basis of Kavaski - Gunton projection operator an explicit non-Markov form of NSO with respect to $\gamma_\alpha(t)$ parameters is obtained and the equivalence of the method to the other methods using boundary conditions for $\rho(t)$ or "mixing" operator is shown. An exact NSO transformation to Markov form with respect to $\gamma_\alpha(t)$ at arbitrary dependence of $V_t$ perturbation on time is made. The generalized kinetic equations not containing the memory with respect to $\gamma_\alpha(t)$ are obtained being convenient for practical application.
1. Introduction

The existing method of theoretical study of irreversible processes [1-3] are based on N.N.Bogoliubov concept [1] of sequential reductions of parameter number necessary for description of nonequilibrium states of macroscopic system in the process of its evolution in time. In accordance with this concept a quasiequilibrium states is determined in the system at $t \gg \tau_0$ ($\tau_0$ - is the chaotization time) that can be characterized by giving average values $\gamma_\alpha(t) = Sp\{\rho(t)\hat{\gamma}_\alpha\}$ varying comparatively slowly in time and generally speaking in space. $\{\gamma_\alpha\}$ is a set of limited linearly independent operators ($\alpha$ is the complex of discrete and continuous indices on which $\hat{\gamma}_\alpha$ operators depend). $\gamma_\alpha(t)$ is generally called the generalized thermodynamical coordinates (GTC) of system. Nonequilibrium statistical operator (NSO) $\rho(t)$ giving a rough description of the system at $t \gg \tau_0$ is, in the general case, a functional depending on operators $\hat{\gamma}_\alpha$ and GTC $\gamma_\alpha(t)$. $\gamma_\alpha(t)$ functions are determined by solution of the closed system of generalized kinetic equations (GKE) obtained by averaging of operator equations of motion for $\hat{\gamma}_\alpha$ over NSO $\rho(t)$.

The choice of $\hat{\gamma}_\alpha$ operators should be made individually for each specific system taking into account the hierarchy of the interactions existing in it.

2. Choice of GTC

Let us consider space-uniform nonequilibrium system with time-dependent Hamiltonian $H_t$:

$$H_t = H_0 + V_t; \quad V_t \equiv V + H_F(t) \ll H_0$$

(2.1)

$H_0$ - is the main Hamiltonian defining a set of operators $\{\hat{\gamma}_\alpha\}$ and $V_t$ contains relatively weak interaction including those with variable external fields (addend $H_F(t)$) that do not affect the choice of operators $\hat{\gamma}_\alpha$.

Generally, the degree of freedom of macroscopic system can be divided into separate quasi-independent groups called subsystems. Then, $H_0$ is the Hamiltonian of free subsystems including as a independent subsystems the effective multipart interaction $H_{eff}$
responsible for chaotization time $\tau_0$; $V$ is the interaction between subsystems. Such situation is realized in the problems of magnetic resonance in solids [4].

At investigation of the kinetics of condensed medium on the basis of the idea of quasiparticles [5], as well as in gases [1] $H_0$ is the Hamiltonian of free quasiparticles and the interaction between them is described by operator $V$. In this case $\tau_0$ is of the order of collision time and does not depend neither on $H_0$, nor on $V$ value.

The main requirement for $\hat{\gamma}_\alpha$, operators is [3]:

$$iL_0\hat{\gamma}_\alpha \equiv \frac{1}{i\hbar}[\hat{\gamma}_\alpha, H_0] = i \sum_\beta \alpha_{\alpha\beta} \hat{\gamma}_\beta \quad (2.2)$$

$\alpha_{\alpha\beta}$ is the matrix of c numbers defined by properties of $H_0$ operator symmetry. For solid spin systems the following requirement should be added to (2.2)

$$[\hat{\gamma}_\alpha, H_{\text{eff}}] = 0. \quad (2.3)$$

The idea of (2.2) and (2.3) conditions is that the set of $\{\hat{\gamma}_\alpha\}$ is formed by the main Hamiltonian $H_0$ independent of $V_t$ perturbation. Operators $\hat{\gamma}_\alpha$ while commutating with $H_0$ are to be closed on themselves, i.e. they should commutate with the effective interaction when it is included into $H_0$, but not necessarily commutate between themselves.

According to (2.1) - (2.3) the evolution of macroscopic parameters $\gamma_\alpha(t)$ in time includes the dynamic change at the expense of $H_0$ (being considered exactly) and $H_F(t) \ll H_0$ (being considered according to the perturbation theory), as well as the relaxation change at the expense of $V \ll H_0$ with relaxation time $\tau_r$, and in accordance with the principles of reduced description $\tau_r \gg \tau_0$.

3. The method of construction of nonequilibrium statistical operator

The simplest method of NSO construction is the application of Liouville equation with infinitively small source [6]:

$$\left\{ \frac{\partial}{\partial t} + iL(t) \right\} \rho(t) = -\epsilon \left\{ \rho(t) - P(t)\rho(t) \right\}; \quad \epsilon \rightarrow +0 \quad (3.1)$$

where Liouville operators are determined by the expression:
\[ L(t) = L_0 + L_v(t); \]
\[ iL_0 A = \frac{1}{i\hbar}[A, H_0]; \]
\[ iL_v(t) A = \frac{1}{i\hbar}[A, V(t)]. \]

Projection operator \( P(t) \) determines the degree of rough description of nonequilibrium states of the system and the structure of NSO \( \rho(t) \) at \( t \gg \tau_0 \). It is convenient to use Kawasaki - Gunton projection operator as a \( P(t) \) \([7]\):

\[ P(t) A = \rho_q(t) S_p A + \sum_\alpha \frac{\partial \rho_q(t)}{\partial \gamma_\alpha(t)} \{ S_p (\gamma_\alpha A) - \gamma_\alpha(t) S_p A \}; \quad (3.2) \]

where

\[ \rho_q(t) = Q_q^{-1} \exp \{- \sum_\alpha F_\alpha(t) \gamma_\alpha \}; \]
\[ Q_q = S_p \exp \{- \sum_\alpha F_\alpha(t) \gamma_\alpha \}; \quad (3.3) \]

\( \rho_q(t) \) is the quasiequilibrium statistical operator depending on \( t \) implicitly through GTC \( \gamma_\alpha(t) \). The functional connection \( F_\alpha(t) \equiv F_\alpha(\gamma_\alpha(t)) \) is determined by matching conditions

\[ \gamma_\alpha(t) = S_p \{ \rho(t) \gamma_\alpha \} = S_p \{ \rho_q(t) \gamma_\alpha \}; \quad (3.4) \]

providing the coincidence of true and quasiequilibrium values of macroscopic parameters and the conjugation of two sets of \( \gamma_\alpha(t) \) and \( F_\alpha(t) \) functions in the sense of nonequilibrium thermodynamics \([2]\).

According to (3.2) and (3.4) \( P(t) \) has the following properties:

\[ P(t) \rho(t) = \rho_q(t); \]
\[ P(t) \frac{\partial \rho(t)}{\partial t} = \frac{\partial \rho_q(t)}{\partial t}; \]
\[ P(t') P(t) A = P(t') A. \quad (3.5) \]

Eq. (3.1) is similar to usual Liouville equation:

\[ \{ \frac{\partial}{\partial t} + iL(t) \} \rho(t) = 0 \quad (3.6) \]
and to the boundary condition of delay type [6,8]

\[ T \exp\{i \int_t^{t+\tau} L(t') dt'\} \rho(t + \tau) \rightarrow_{\tau \to -\infty} T \exp\{i \int_t^{t+\tau} L(t') dt'\} \rho_q(t + \tau). \] (3.7)

Thus, the introduction of infinitively small source into Liouville equation is the convenient method of selection of delayed solution of this equation that depends on \( \gamma_\alpha(t) \) and satisfies the boundary condition in (3.7).

In the Appendix the equivalence of the boundary condition (3.7) and the mixing operations are shown:

\[ \exp(iL_0 \tau) \rho(t) \rightarrow_{\tau \to -\infty} \exp(iL_0 \tau) \rho(\gamma(t)), \] (3.8)

that is used in the method [3,9].

This fact is very remarkable the more so that we have the significant difference in conditions (3.7) and (3.8). If in (3.7) evolution of the system is considered from moment \( t \) to moment \( t + \tau \) along the phase trajectory, i.e. with the whole Hamiltonian \( H_t \) during which are changed both the dynamical variables (multiplier \( T \exp\{i \int_t^{t+\tau} L(t') dt'\} \)), and the macroscopic parameters \( (\gamma_\alpha(t) \rightarrow \gamma_\alpha(t + \tau)) \), in (3.7) the mixing operation describing a free evolution of the system takes place at fixed values of \( \gamma_\alpha(t) \).

The solution of Eq. (3.1) has the following form [6,8]:

\[ \rho(t) = \rho_q(t) - \int_{-\infty}^{0} d\tau e^{i\tau} T \exp\{i \int_t^{t+\tau} L(t') dt'\} \left( \frac{\partial \rho_q(t + \tau)}{\partial \tau} \right) + iL(t + \tau) \rho_q(t + \tau). \] (3.9)

The use of explicit form of NSO (3.9) in the Appendix is difficult because of its complex structure. In this respect the integral equation for \( \rho(t) \) [10], derived in the absence of variable fields for \( \gamma_\alpha \) operators satisfying (2.2) is much easier:

\[ \rho(t) = \rho_q(t) - \int_{-\infty}^{0} d\tau e^{i(\gamma L_0 + L_v)\tau} (1 - P_R(t + \tau)) iL_v(t + \tau) \rho(t + \tau), \] (3.10)

where

\[ P_R(t)A = \sum_\alpha \frac{\partial \rho_q(t)}{\partial \gamma_\alpha(t)} Sp(\gamma_\alpha A) - \]
is the Robertson projection operator [11]. According to (3.2), $P_R(t)A = P(t)A$, if $SpA = 0$.

At $\epsilon = 0$ Eq. (3.10) coincides with the equation obtained by the other method [12] when studying the system evolution under the influence of external fields variables assuming that at $\tau \to -\infty$ the equilibrium condition of the system was disturbed by adiabatic application of variable field.

In (3.9) and (3.10) $\rho(t)$ is non-Markov functional of $\gamma_\alpha(t)$ as it depends on all values of $\gamma_\alpha(t')$ $t' \leq t$. As a consequence, the non-Markov integral-differential generalized kinetic equations are obtained even in the absence of high-frequency fields ($H_F(t) = 0$) [2]:

$$\frac{\partial \gamma_\alpha(t)}{\partial t} = Sp\gamma_\alpha \frac{\partial \rho(t)}{\partial t} = Sp\rho(t)iL(t)\gamma_\alpha \equiv L_\alpha(t),$$  \hspace{1cm} (3.11)

where $L_\alpha(t)$ is the collision integral.

On the other hand, in accordance with the requirement of the completeness of the reduced description of irreversible processes a nonequilibrium condition and hence $\rho(t)$ at some moment of $t$ (from macroscopic point of view) i.e. for $t \gg \tau_0$, should be determined by giving $\gamma_\alpha(t)$ parameters at the same moment of time. In particular problems the memory seems to be insignificant due to the use of operator with (2.2) and (2.3) properties as $\gamma_\alpha$ operators and to the weak interactions $V_t$ [4]. In stationary case $V_t = V \neq f(t)$, as it is shown in [13], one can, in principle, obtain Markov presentation of NSO in any finite order with respect to $V$ by reconstruction of a number of perturbation theories with respect to weak interaction $V$ [10].

Taking into account that in widely and successfully used methods of GKE construction the Markov character of NSO $\rho(t)$ dependence on $\gamma_\alpha(t)$ is supposed from the very beginning [1,3] it is more natural to formulate the Markov form of NSO II method [6] in general form without using a definite order of perturbation theory for $V_t$. The limitation of the class of Eq. (3.1) solutions to Markov type eliminates the difficulties in solution of non-Markov equations (3.10) in high orders of perturbation theory with respect to $V_t$. 

4. Conversion of NSO to Markov form

Let us introduce the operator of shift in time

$$\exp\left\{ \tau \frac{\partial}{\partial \tau} \right\} \varphi (t) \equiv \sum_{n=0}^{\infty} \frac{\tau^n}{n!} \frac{\partial^n}{\partial t^n} \varphi (t) = \varphi (t + \tau).$$

Then Eq. (3.10) has the following form:

$$\rho (t) = \rho (\gamma (t), t) - \int_{-\infty}^{0} d\tau e^{(\epsilon + iL_0)\tau} e^{\tau \frac{\partial}{\partial \tau}} \{ (1 - P_R(t)) iL_v(t) \rho(t) \}. \quad (4.1)$$

Let us proceed from the superposition

$$\rho (t) \equiv \rho (\gamma (t), t); \quad t \gg \tau_0, \quad (4.2)$$

assuming that $\rho(t)$ at $t \gg \tau_0$ depends on $t$ not only through $\gamma_\alpha(t)$ value at the same moment of $t$, but by $V_t$.

Note, that the time dependence of NSO just of such kind is obtained as a result of direct reconstruction of a number of perturbation theories [13], thus the supposition (4.2) can be considered as a mathematical formulation of the possibility to construct Markov with respect to $\gamma_\alpha(t)$ NSO expansion into series with respect to $V_t$ perturbation. In this case the effect of $\partial/\partial t$ operator on arbitrary Markov type $f (\gamma (t), t)$ functional of $\gamma_\alpha(t)$ is determined by the relation:

$$\frac{\partial}{\partial t} f (\gamma (t), t) = \left( \sum_\alpha \frac{\partial \gamma_\alpha (t)}{\partial t} \frac{\partial}{\partial \gamma_\alpha (t)} + \frac{\tilde{\partial}}{\partial t} \right) f (\gamma (t), t) \equiv (D(\gamma (t), t) + \frac{\tilde{\partial}}{\partial t}) f (\gamma (t), t), \quad (4.3)$$

where $\frac{\tilde{\partial}}{\partial t}$ means the partial derivative with respect to real time included in $f (\gamma (t), t)$ functional.

Differentiating (3.4) with respect to time and using (3.1), (2.2) and (3.5), we obtain GKE

$$\frac{\partial \gamma_\alpha (t)}{\partial t} = i \sum_\beta a_{\alpha \beta} \gamma_\beta (t) +$$
where $L_\alpha$ is the collision integral of Markov type with respect to $\gamma_\alpha(t)$.

According to (4.3) we can write

$$D(\gamma(t), t) = \sum_\alpha L_\alpha(\gamma, t) \frac{\partial}{\partial \gamma_\alpha} = D_0(\gamma) + D_v(\gamma, t);$$

where

$$D_0(\gamma) = i \sum_{\alpha, \beta} a_{\alpha \beta} \gamma_\beta \frac{\partial}{\partial \gamma_\alpha};$$

$$D_v = \sum_\alpha Sp(\rho(\gamma, t)iL_v \gamma_\alpha) \frac{\partial}{\partial \gamma_\alpha}. \quad (4.5)$$

Introducing the symbols:

$$B \equiv \rho(\gamma, t) - \rho_q(\gamma);$$

$$A \equiv -(1 - P_R(\gamma))iL_v(t)\rho(\gamma, t);$$

$$H \equiv \frac{1}{i}(\epsilon + iL_0 + D_0(\gamma));$$

$$U \equiv \frac{1}{i}(D_v(\gamma, t) + \frac{\hat{\partial}}{\partial t}). \quad (4.6)$$

in view of Eqs. (4.2), (4.3), (4.5) and the rearrangement ability of $(\epsilon + iL_0)$ and $D(\gamma, t)$, operators, Eq. (4.1) can be written as:

$$B = \int_{-\infty}^{0} d\tau e^{i(H + U)\tau} A. \quad (4.7)$$

Eq. (4.7) is equivalent to integral equation \[3\]

$$B = \int_{-\infty}^{0} d\tau e^{iH\tau}(A - iUB). \quad (4.8)$$

In previous notations, taking into account that $\exp(\tau D_0(\gamma))$ operator describes free evolution of $(V_t = 0)$ from $t$ moment to $t + \tau$ moment at which according to (4.4) $\gamma_\alpha(t) \rightarrow \gamma_\alpha(t + \tau) = (e^{i\tau \gamma(t)})_\alpha = e^{\tau D_0(\gamma)} \gamma_\alpha(t)$ Eq. (4.8) takes the following form:

$$\rho(\gamma, t) = \rho_q(t) - \int_{-\infty}^{0} d\tau e^{(\epsilon + i\gamma(t))\tau}(iL_v(t)\rho(\gamma, t) +$$

$$+ \sum_\alpha Sp(\rho(\gamma, t)iL_v \gamma_\alpha) \frac{\partial}{\partial \gamma_\alpha})$$
\[
+ \sum_{\alpha} \frac{\partial \rho(\gamma,t)}{\partial \gamma_{\alpha}} \text{Sp} \{\rho(\gamma,t)iL_v(t)\gamma_{\alpha}\} + \frac{\partial}{\partial t} \rho(\gamma,t)\} \rightarrow e^{i\alpha \gamma}, \tag{4.9}
\]

where the equality

\[
D_v(\gamma,t) \rho_q(\gamma) = \sum_{\alpha} \frac{\partial \rho_q(\gamma)}{\partial \gamma_{\alpha}} \text{Sp} \{\rho(\gamma)iL_v(t)\gamma_{\alpha}\} = -P_R(\gamma)iL_v(t)\rho(\gamma,t).
\]
is used.

Similarly, instead of (4.6) we use the notations (symbols):

\[
B \equiv \rho(\gamma,t) - \rho_q(\gamma);
\]

\[
A \equiv -(1 - P_R(\gamma))iL_v(t)\rho(\gamma,t);
\]

\[
H = \frac{1}{i}(\epsilon + iL_0 + D_0(\gamma) + \frac{\partial}{\partial t});
\]

\[
U = \frac{1}{i}D_v(\gamma,t), \tag{4.10}
\]

we obtain:

\[
\rho(\gamma,t) = \rho_q(\gamma) - \int_{-\infty}^{0} d\tau e^{(\epsilon+iL_0)\tau} \{iL_v(t+\tau)\rho(\gamma,t+\tau) +
+ \sum_{\alpha} \frac{\partial \rho(\gamma,t+\tau)}{\partial \gamma_{\alpha}} \text{Sp} \rho(\gamma,t+\tau)iL_v(t+\tau)\gamma_{\alpha}\} \rightarrow e^{i\alpha \gamma}. \tag{4.11}
\]

It is easily seen that Exps. (4.9) and (4.11) are strictly equivalent and automatically satisfy the matching conditions (3.4).

When \(\epsilon = 0\), (4.9) coincides with the equation obtained directly from Liouville equations using boundary conditions (3.8) in low-frequency region \(\omega \tau_0 \ll 1\) of variable field [3], and Eq. (4.11) coincides with the equation derived by similar method for arbitrary values of \(\omega \tau_0\) parameter [14]. In stationary condition \((H_F(t) = 0)\), when NSO \(\rho(t)\) does not depend explicitly on time at \(\epsilon = 0\) Eqs. (4.9) and (4.11) coincides with the basic equation of the method [9]. The same result assuming \(\rho(t) = \rho(\gamma(t))\) at \(t \gg \tau_0\) can be obtained directly from Eq. (3.1) [15].

In our method Eqs. (3.10), (4.9) and (4.11) are similarly applicable at arbitrary values of \(\omega_0 \tau\) parameter. Nevertheless, in the low-frequency region when \(\omega \tau_0 \ll 1\) and
correspondingly \( \frac{\partial \rho(\gamma,t)}{\partial t} \sim \omega \tau_0 \) term is small it is convenient to use Eq. (4.9) and at high frequencies \( \omega \tau_0 \geq 1 \) is preferable to use Eq. (4.11).

In general case at arbitrary \( \omega \tau_0 \) GKE (4.4) are differential with respect to \( t \), i.e. belong to Markov type, though they contain the memory with of respect to variable field. At \( \omega \tau_0 \ll 1 \) the memory with respect to field disappears and the evolution of the system in time in the variable field is strictly Markov type.

5. Discussion of results

Let us discuss the conditions of applicability of the obtained equations. According to (3.6) \( \rho(-\infty) = \rho_0(-\infty) = \rho_0 \) (\( \rho_0 \) - is the equilibrium statistical operator of the system). To form the quasiequilibrium state \( \sim \tau_0 \) time is required. Therefore NSO \( \rho(\gamma,t) \) and Eqs. (3.10), (4.9), (4.11) describe the system at \( t \gg \tau_0 \).

Let us assume that in remote part the system was in equilibrium \( \rho(-\infty) = \rho_0 \) and then the equilibrium was disturbed by adiabatic application of variable fields. As is shown in [3,12] at such boundary condition the limitation of \( t \gg \tau_0 \) is removed and Eq. (3.10) and hence Eqs. (4.9) and (4.11) following from it describe the system adequately all \( t \) time.

As for the frequencies \( \omega \) and amplitudes \( \omega_1 \) of variable fields Eqs.(3.10), (4.9) and (4.11) are applicable at arbitrary frequencies and at the amplitudes for which \( H_f(t) \ll H_0 \).

Macroscopic parameters \( \gamma_\alpha(t) \) usually are introduced for description of nonequilibrium states of systems, the Hamiltonian of which does not depend on time. At the action of variable fields the time-dependence of Hamiltonian is eliminated by the transition into rotating coordinate system [16] or by considering the fields from quantum point of view [17] and only after this \( \gamma_\alpha(t) \) is introduced. When \( \gamma_\alpha \) operators commutate with \( H_0 \) i.e. \( a_{\alpha\beta} \equiv 0 \) such approach preserves the common thermodynamic sense of \( \gamma_\alpha(t) \) values and is the most consistent. But such approach is not always applicable, therefore one should discuss the problem of possibility to use \( \gamma_\alpha(t) \) parameters in general case.

First, let us assume that \( a_{\alpha\beta} \equiv 0 \). In the low-frequency region \( \gamma_\alpha(t) \) parameters, being the slowly changing time functions preserve the common thermodynamic sense. At each
instant of \( t \) time the system is "adjusted" to the instant value of Hamiltonian \( H_t \) (2.1). Then the whole difference from the stationary case is reduced only to that for \( t \gg \tau_0 \) the statistical operator \( \rho(t) \) depends on \( t \) not only through \( \gamma_\alpha(t) \), but explicitly through the variable field \( F(t) \) and its derivatives \( \dot{F}(t), \ddot{F}(t), \ldots \) [3]. As it mentioned in [3], for \( \omega \tau_0 \ll 1 \) the kinetic processes are in fact the Markov type and (4.9) is obtained from (3.10) by direct expansion of \( V_{\tau} \) and \( \gamma_\alpha(t+\tau) \) values into power series \( \tau \). In our aforementioned approach, Eqs.(3.10) and (4.9) are strictly equivalent for any values of \( \omega \tau_0 \) parameter.

In the high-frequency region \( \omega \tau_0 \geq 1 \) the non-Markov character of kinetic processes, taking place in the system under the action of variable fields will manifest itself. In this case the expansion in terms of \( \omega \tau_0 \) parameter seems impossible. \( \gamma_\alpha(t) \) parameters have no longer the direct thermodynamic sense as they contain the rapid, but low-amplitude (because \( H_F(t) \ll H_0 \)) dynamic change induced by high-frequency field. Nevertheless, \( \gamma_\alpha(t) \) parameters can be still used for description of quasiequilibrium states, as, according to (3.2), owing to the ”mixing” action of \( H_0 \), the system will have time to be ”adjusted” to the instant nonequilibrium values of \( \gamma_\alpha(t) \) parameters.

When \( a_{\alpha\beta} \neq 0 \) and \( V_t = 0 \), \( \gamma_\alpha(t) \) values in accordance with (4.4) are changed by the law \( \gamma(t) = e^{iat} \gamma(0) \) with arbitrary frequencies determined by eigenvalues of \( (e^{iat})_{\alpha\beta} \) matrices. Therefore, \( \gamma_\alpha(t) \) are not ”slow” thermodynamic values even in the absence of variable fields. However, it is remarkable that in the general case \( a_{\alpha\beta} \neq 0, \omega \tau_0 \geq 1 \) the ”adjusting” of the system to the instant values \( \gamma_\alpha(t) \) takes place and the dependence of \( \rho(\gamma(t),t) \) on \( \gamma_\alpha(t) \), as well as Eq. (4.11), are of Markov character with respect to \( \gamma_\alpha(t) \), though they contain the memory with respect to variable field.

Conclusion

The carried out study shows the full equivalence of the boundary condition (3.7) and mixing operation (3.8). Thus, we prove the strict equivalence of the method [3,9,12] to the variety of NSO method [6] based on Liuville equation with infinitively small source (3.1) and \( \dot{\gamma}_\alpha \) operators with (2.2) properties.

The main conclusion of the work is that the method NSO II [6] can be formulated in
Markov form with respect to $\gamma_\alpha(t)$ parameters even in the presence of high-frequency fields. As a result, the use of high order perturbation theory with respect to small interactions in the system is considerably facilitated.
Appendix

Let us show the equivalence of boundary condition (3.7) and mixing operation (3.8). Liuville equation (3.5) can be written as

\[
\left( \frac{\partial}{\partial t} + iL_0 \right) \delta \rho(t) = -(1 - P_R(t))iL_v(t)\rho(t); \delta \rho = \rho - \rho_q. \tag{A1}
\]

Let us multiply (A1) by integrating factor \( \exp(iL_0 t) \) and integrate it from \(-\infty\) to \(t\).

Note, that the solution of Eq. (3.1) has the [6,8]:

\[
\rho(t) = \rho_q(t) - \int_{-\infty}^{t} d\tau e^{i\tau T} \exp \left\{ i \int_{t}^{t+\tau} L(t')dt' \right\} \left( \frac{\partial \rho_q(t + \tau)}{\partial \tau} + iL(\tau)\rho_q(t + \tau) \right) = \\
= \rho_q(t) - \int_{-\infty}^{0} d\tau e^{i\tau T}(t, t + \tau)(1 - P_R(t + \tau))iL(t + \tau)\rho_q(t + \tau), \tag{A2}
\]

where

\[ T(t, t_1) = T \exp \left\{ - \int_{t_1}^{t} (1 - P_R(t'))iL(t')dt' \right\}, \]

and \( P_R(t) \) is determined in the main text (see (3.10)).

Using (2.2) and the relation [3,8],

\[
e^{-iL_0\tau} \rho_q(\gamma(t)) = \rho_q(e^{2i\alpha\tau}\gamma(t)), \tag{A3}
\]

we obtain:

\[ e^{iL_0t} \delta \rho(t) = - \int_{-\infty}^{t} dt'e^{iL_0t'}(1 - P_R(t'))iL_v(t')\rho(t'). \tag{A4}\]

Taking into account that according to (3.8),

\[ \lim_{\tau \to -\infty} e^{iL_0\tau}(\rho(\tau) - \rho_q(\tau)) = 0, \]

after simple transformation of (A4) we have

\[ \rho(t) = \rho_q(t) - \int_{-\infty}^{0} d\tau e^{iL_0\tau}(1 - P_R(t + \tau))iL_v(t + \tau)\rho(t + \tau). \tag{A5}\]

(A5) coincides with (3.10) at \( \epsilon = 0 \). The forming factor \( e^{i\tau} \) does not affect the integral convergence [13,15] included in Eq. (3.10) and Eqs. (3.6), (3.8) and (3.6), (3.7) are fully equivalent as they result in coinciding integral equations (3.10) and (A5).
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