Dynamics of particle transfer in a symmetric double-well potential has been investigated. In restriction to two-level system, the convolution form of generalized master equation with retention of off-diagonal matrix elements has been solved on non-Markovian level as well in Markov approximation. It has been shown that subsystem dynamics crucially depends on interplay of three variables, correlation time of an environment, dephasing time and coherent transfer time. The character of dynamics then varies from damped oscillations through exponential decay and incoherent relaxation. It has been shown that on non-Markovian level, under some circumstances, the particle transfer is governed by the dynamics of slow environment.

1. INTRODUCTION

The most important dynamic phenomena in physics, chemistry and biochemistry are connected with simple elementary processes of energy, electron or proton transfer. Theoretical description and understanding of these processes is a non-trivial matter. Different techniques have been used starting with formal kinetic equations through more sophisticated quantum-statistical methods. Since the works of Nakajima and Zwanzig [1], new possibilities permitting a microdynamics description with subsequent projection of relevant information have been offered.

The equation of motion for reduced density matrix has been derived from Liouville – von Neumann equation in the form,

$$\mathcal{D}\rho(t) = -i\mathcal{L}\rho(t) - \int_0^t \mathcal{L} e^{-i(1-\mathcal{D})\mathcal{L}t}(1 - \mathcal{D})\mathcal{L}\rho(t - \tau) \, d\tau$$

where $\rho(t)$ is the density matrix of total (composite) system, $\mathcal{L}$ is Liouville superoperator corresponding to the Hamiltonian of the total system and $\mathcal{D}$ is projection superoperator projecting out the relevant information. Depending on the form of projection superoperator $\mathcal{D}$, one gets different forms of generalized master equation (GME). Choosing for instance,

$$(\mathcal{D}\rho)_{Aa,Bb} = \delta_{Aa,Bb}p_a \sum_{c} Q_{Ac,Ac}$$

with $p_a$ being arbitrary constant satisfying $\sum_a p_a = 1$, the GME is of the form
\[ \dot{\sigma}_{AA}(t) = \sum_{B} \int_{0}^{t} W_{AB}(t - \tau) \sigma_{BB}(\tau) \, d\tau = \sum_{A(\neq B)} \int_{0}^{t} (W_{AB}(t - \tau) \sigma_{BB}(\tau) - W_{BA}(t - \tau) \sigma_{AA}(\tau)) \, d\tau. \]

The eq. (2) is derived under assumptions of initial time diagonality of \( \sigma(0) \), and statistical independency of the subsystem and environment which is in thermal equilibrium at \( t = 0 \), i.e., \( \rho(0) = \rho_{\text{eq}} \). This form of the GME has been used mainly in solid state physics at the studies of different kinetic phenomena\(^1\). The physical meaning of particular terms is the following:

- \( \sigma_{AA} \) — diagonal element of the reduced density matrix that in a local basis \( \{A\} \) represents site probability density,
- \( W_{AB}(t) = \sum (\mathcal{L} e^{-i(1-\beta)\mathcal{L}t})_{ABA,Ab,b} p_b \) is matrix element of memory function.

The assumption of very short memory (the extreme case is, \( W_{AB}(t) = W_{AB} \delta(t) \)) turns the GME (2) into the well known form of Pauli master equation (PME)

\[ \dot{\sigma}_{AA}(t) = \sum_{A(\neq B)} (W_{AB} \sigma_{BB}(t) - W_{BA} \sigma_{AA}(t)). \]

A similar way in “deriving” eq. (3) from (2) even for finite memory time is based on the assumption that for the decay time of memory function much shorter than the characteristic time of the subsystem dynamics, the Markovian approximation to the GME,

\[ \int_{0}^{t} W_{AB}(t - \tau) \sigma_{BA}(\tau) \, d\tau \approx \int_{0}^{\infty} W_{AB}(\tau) \, d\tau \sigma_{BA}(t) \]

is justified, and the GME (2) and PME (3) are equivalent at least in long time domain\(^2\).

It was proved in the theory of dynamic semigroup [4] that the exact equivalence on the whole time scale between the GME and PME takes place only for two extreme cases:

1. weak coupling limit — zero coupling with an environment,
2. singular reservoir limit — an environment without memory.

As far as the equivalence between the GME (2) and PME (3) in long time domain for finite coupling and memory is concerned, it was shown recently [5] that Markovian and non-Markovian dynamics are substantially different. A note is worth making here regarding the fact that the GME as discussed in [5] has been in diagonal form — eq. (2).

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\(^1\) For general review see [2].

\(^2\) The approximation is discussed in almost any publication concerning the physics of open systems, see for instance [3].