Perturbation theory for Lindblad superoperators for interacting open quantum systems

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We study the dynamics of interacting open quantum subsystems. Interactions merge these subsystems into a unified system. It is often believed that the Lindblad superoperator of the unified system is the sum of the Lindblad superoperators of the separate subsystems. Such an approach, however, results in a violation of the second law of thermodynamics. To avoid a cumbersome direct derivation of the correct superoperator from first principles, we develop a perturbation theory based on using Lindblad superoperators of separate subsystems, which are assumed to be known. Using interacting two-level systems as an example, we show that, starting with a certain order of the perturbation theory, the second law of thermodynamics holds. We demonstrate that the theory developed can be applied to the problems of quantum transport.

I. INTRODUCTION

Recently, the study of open quantum systems has experienced rapid growth connected to studies of interacting arrays of qubits [1], ensembles of quantum dots and molecules [2], and systems of atoms coupled with resonators [3–5]. Such systems are open in the sense that they interact with the environment.

The exact dynamics of an open quantum system can only be obtained for a small number of problems [6–10]. Therefore, various approximate methods are used [11–13]. One of the most common is the method of the Lindblad-Gorini-Kossakowski-Sudarshan (LGKS) equation [14,15]. This method implies that both the system and the reservoir have separated Hamiltonians and that the coupling between them can be expressed as the interaction Hamiltonian. The derivation of the LGKS equation involves the use of the von Neumann equation for the system-reservoir density matrix and the subsequent elimination of the reservoir degrees of freedom. The states of the latter are assumed to be unchangeable during the evolution of the system. After such elimination, the evolution operator of the system's density matrix includes the Hamiltonian and Lindblad superoperators [16]. These Lindblad superoperators are constructed from the product of the transition operators between the system eigenstates. The transitions occur under the influence of the reservoirs. The transition rates are calculated according to the Fermi golden rule [17].

Although the general theory of deducing the LGKS equation is well developed [16], a direct way of constructing Lindblad superoperators requires knowledge of the exact system eigenstates and eigenenergies [18,19]. For a unified system containing interacting subsystems, the complexity of the calculation of the eigenstates and eigenenergies of the unified system grows exponentially with the number of subsystems. Therefore, for a unified system, the direct approach is impractical.

It is desirable to express the Lindblad superoperator of the unified system through the Lindblad superoperators of subsystems. The key issue is that the eigenstates of the unified system are no longer a direct product of the eigenstates of isolated subsystems. Consequently, the transition operators between eigenstates of the unified system that appear in the Lindblad superoperator are no longer equal to direct products of the transition operators of subsystems, and the Lindblad superoperator of the unified system is not equal to the sum of the Lindblad superoperators for isolated subsystems [17–20]. However, in many cases it is believed that even if the whole Hamiltonian includes the interactions between subsystems, all the relaxation processes in the unified system are the same as for isolated subsystems [2,21–32]. Such an approximation is called the local approach. Mathematically, it implies that the Lindblad superoperator of the unified system is the sum of Lindblad superoperators of the isolated subsystems. One might suppose that the local approach will only lead to minor quantitative differences from the exact solution. Unfortunately, this is not the case. In particular, the local approach may result in the violation of the second law of thermodynamics [20,33]. Recently, considerable attention has been devoted to a detailed comparison between the dynamics predicted by the local approach and the exact Lindblad superoperators for a number of systems [34–41], including interacting two-level systems [42], harmonic oscillators [43], and optomechanical systems [44]. In [45] it was shown that the second law of thermodynamics can be restored if the environment is divided into an ensemble of identically prepared auxiliary systems, which interact

sequentially with an individual subsystem for an infinitesi-
mally short time. However, for the permanent interaction of
the system and reservoirs the fulfillment of the second law is
not guaranteed.

In this paper we develop a perturbative method for building
the Lindblad superoperator of a system comprised of inter-
acting subsystems. The perturbation theory developed for the
Lindblad superoperator is based on the construction of the
transition operators that appear in this Lindblad superoperator.
We demonstrate that the transition operators can be found
from the interaction of the Hamiltonian of the reservoir and
the system by employing the Heisenberg equation of motion.
At each step of the perturbation theory the system of the
Heisenberg equations for the transition operator is linear and
closed, can be solved exactly. The developed method ensures
the fulfillment of the principles of thermodynamics. This ap-
proach permits us to express the Lindblad operator of the
unified system through the linear combination of products of
the transition operators of the separate subsystems. Using in-
teracting two-level systems as an example, we find the lowest
order of the perturbation series that ensures the fulfillment of
the second law of thermodynamics.

II. PERTURBATION THEORY APPROACH FOR OBTAINING THE LINDBLAD SUPEROPERATORS

We consider a system described by the Hamiltonian

$$\hat{H} = \hat{H}_S^{(\mathrm{is})} + \varepsilon\hat{W} + \hat{H}_{SR} + \hat{H}_R, \tag{1}$$

where $\hat{H}_S^{(\mathrm{is})} = \sum_\alpha \hat{H}_{S\alpha}^{(\mathrm{is})}$ is the Hamiltonian of the system com-
prised of isolated subsystems, which are enumerated by the
subscript α and described by the Hamiltonians $\hat{H}_{S\alpha}^{(\mathrm{is})}$; each
αth subsystem interacts with its own reservoir described by
the operator $\hat{H}_{R\alpha}$, so the Hamiltonian for the reservoir of the
whole system is $\hat{H}_R = \sum_\alpha \hat{H}_{R\alpha}$. The Hamiltonians $\hat{H}_{S\alpha}^{(\mathrm{is})}$ and
$\hat{H}_{R\alpha}$ depend only on the subsystem and reservoir degrees of
freedom, respectively. The interaction of the αth subsystem
and its reservoir is described by the operator $\hat{H}_{SR\alpha}$; so for the
whole system Hamiltonian for the interaction with reservoirs
is $\hat{H}_{SR} = \sum_\alpha \hat{H}_{SR\alpha}$. The interaction between the subsystems is
governed by the Hamiltonian $\varepsilon\hat{W} = \varepsilon \sum_{\alpha_1\alpha_2} \hat{W}_{\alpha_1\alpha_2}$, where ε is
a small dimensionless parameter. For example, in the case of
interacting two-level systems, ε is the dimensionless coupling
constant between them. For simplicity, we assume that ε is
the same for all subsystems. We assume that the Hamiltonian
$\hat{H}_{S\alpha}^{(\mathrm{is})}$ of the αth isolated subsystem has known nondegenerate
eigenstates $|k_{\alpha i}^{(\mathrm{is})}\rangle$ and eigenfrequencies $\omega_{\alpha i}^{(\mathrm{is})}$ enumerated by
the subscript i.

Usually, it is assumed that the Hamiltonian of the interac-
tion between a system and a reservoir has the form [16,17]

$$\hat{H}_{SR\alpha} = \hbar\lambda_\alpha \hat{S}_\alpha \hat{R}_\alpha, \tag{2}$$

where λ_α is the interaction constant and $\hat{S}_\alpha$ and $\hat{R}_\alpha$ are the
operators of the subsystem and its reservoir, respectively.
For example, for a single two-level atom, $\alpha = 1$, interacting
with the electromagnetic field of free space, the Hamiltoni-
ans are $\hat{H}_{S\alpha}^{(\mathrm{is})} = \hbar\omega_0\hat{\sigma}^\dagger\hat{\sigma}$, $\hat{H}_{R\alpha} = \sum_{\mathbf{k},\eta} \hbar\omega_{\mathbf{k}}\hat{a}_{\mathbf{k}\eta}^\dagger\hat{a}_{\mathbf{k}\eta}$, and $\hat{H}_{SR\alpha} = \sum_{\mathbf{k},\eta} \hbar\Omega_{\mathbf{k}\eta}(\hat{a}_{\mathbf{k}\eta}^\dagger + \hat{a}_{\mathbf{k}\eta})(\hat{\sigma}^\dagger + \hat{\sigma})$, where ω_0 is the transition

frequency of the atom, $\omega_{\mathbf{k}}$ is the frequency of a photon with
the wave vector $\mathbf{k}$ and the polarization η, and $\Omega_{\mathbf{k}\eta}$ is the
coupling constant between the atom and the photon with
the wave number $\mathbf{k}$ and polarization η. The operator $\hat{\sigma}$ is the
transition operator from the excited state to the ground state
of the two-level atom; the operator $\hat{a}_{\mathbf{k}\eta}$ is the annihilation
operator of the photon with the wave vector $\mathbf{k}$ and polarization
η. In this example the operator $\hat{S}_\alpha$ is $(\hat{\sigma}^\dagger + \hat{\sigma})$, λ_α is $\Omega_{\mathbf{k}_0\eta_0}$, and
$\hat{R}_\alpha$ is $\Omega_{\mathbf{k}\eta}(\hat{a}_{\mathbf{k}\eta}^\dagger + \hat{a}_{\mathbf{k}\eta})/\Omega_{\mathbf{k}_0\eta_0}$, where $\mathbf{k}_0$ and η_0 are the wave
vector and the polarization of the free-space mode for which
$\Omega_{\mathbf{k}_0\eta_0} \neq 0$, respectively.

The von Neumann equation for the density matrix $\hat{\rho}(t)$ of
the unified system and the reservoir follows from the Hamil-
tonian (1),

$$\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{i}{\hbar}[\hat{\rho}(t), \hat{H}_S + \hat{H}_{SR} + \hat{H}_R], \tag{3}$$

where we introduced the Hamiltonian of the unified system
$\hat{H}_S = \hat{H}_S^{(\mathrm{is})} + \varepsilon\hat{W}$. The exclusion of the reservoir degrees of
freedom according to the standard procedure [16,20,46,47]
demands the transition of the equation into the interaction
representation, with the new density matrix defined as

$$\hat{\tilde{\rho}}(t) = \exp\left(i\frac{\hat{H}_S + \hat{H}_R}{\hbar}t\right)\hat{\rho}(t)\exp\left(-i\frac{\hat{H}_S + \hat{H}_R}{\hbar}t\right). \tag{4}$$

The von Neumann equation for the new density matrix $\hat{\tilde{\rho}}(t)$
can be obtained from Eq. (3),

$$\frac{\partial\hat{\tilde{\rho}}(t)}{\partial t} = \frac{i}{\hbar}\left[\hat{\tilde{\rho}}(t), \sum_\alpha \hat{\tilde{H}}_{SR\alpha}(t)\right], \tag{5}$$

where the operator $\hat{\tilde{H}}_{SR\alpha}(t)$ is the Hamiltonian $\hat{H}_{SR\alpha}$, given by
Eq. (2), in the interaction representation

$$\begin{aligned}
\hat{\tilde{H}}_{SR\alpha}(t) &= \exp\left(i\frac{\hat{H}_S + \hat{H}_R}{\hbar}t\right)\hat{H}_{SR\alpha}\exp\left(-i\frac{\hat{H}_S + \hat{H}_R}{\hbar}t\right) \\
&= \hbar\lambda_\alpha \exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha\exp(-i\hat{H}_S t/\hbar)\exp(i\hat{H}_R t/\hbar)\hat{R}_\alpha \\
&\quad\times \exp(-i\hat{H}_R t/\hbar). \tag{6}
\end{aligned}$$

The standard procedure implies the averaging over the
reservoir degrees of freedom in Eq. (5) [18,19]. This aver-
aging procedure is similar to the well-known rotating-wave
approximation in quantum optics [48,49]. The averaging over
the reservoir degrees of freedom in Eq. (5) leads to the master
equation for the system density matrix of the unified system
$\hat{\tilde{\rho}}_S(t) = \mathrm{Tr}_R[\hat{\tilde{\rho}}(t)]$ [18,19]:

$$\frac{d\hat{\tilde{\rho}}_S(t)}{dt} = \hat{L}_{\mathrm{ex}}[\hat{\tilde{\rho}}_S(t)]. \tag{7}$$

The influence of the reservoir on the unified system in
Eq. (7) reduces to the Lindblad superoperator $\hat{L}_{\mathrm{ex}}[\hat{\tilde{\rho}}_S(t)]$. To
derive this Lindblad superoperator $\hat{L}_{\mathrm{ex}}[\hat{\tilde{\rho}}_S(t)]$, according to
the standard algorithm [18,19], we should find the explicit

expression for the operators $\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar)$ in the form

$$\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar)$$
$$= \sum_{ij} \langle k_i|\hat{S}_\alpha|k_j\rangle |k_i\rangle\langle k_j| \exp(i\Delta\omega_{ij}t), \qquad (8)$$

where $\Delta\omega_{ij} = \omega_j - \omega_i$ and ω_j are eigenfrequencies corresponding to the eigenstates $|k_j\rangle$ of the Hamiltonian $\hat{H}_S$. Once the series (8) is found, one can apply the standard procedure and obtain the Lindblad superoperator

$$\hat{L}_{\mathrm{ex}}[\hat{\bar{\rho}}_S(t)] = \sum_\alpha \sum_{ij} \lambda_\alpha^2 G_\alpha(\Delta\omega_{\alpha ij})\left\{\left[\hat{S}_{\Delta\omega_{\alpha ij}}, \hat{\bar{\rho}}_S(t)\hat{S}_{\Delta\omega_{\alpha ij}}^\dagger\right]\right.$$
$$\left. + \left[\hat{S}_{\Delta\omega_{\alpha ij}}\hat{\bar{\rho}}_S(t), \hat{S}_{\Delta\omega_{\alpha ij}}^\dagger\right]\right\}, \qquad (9)$$

where we introduced the operators

$$\hat{S}_{\Delta\omega_{\alpha ij}} = \langle k_i|\hat{S}_\alpha|k_j\rangle |k_i\rangle\langle k_j| \qquad (10)$$

and the function $G_\alpha(\Delta\omega_{\alpha ij})$ is defined as

$$G_\alpha(\Delta\omega_{\alpha ij}) = \int_0^{+\infty} \mathrm{Tr}_R[\hat{R}_\alpha^\dagger \exp(i\hat{H}_R t/\hbar)\hat{R}_\alpha \exp(-i\hat{H}_R t/\hbar)]$$
$$\times \exp(i\Delta\omega_{\alpha ij}t)dt. \qquad (11)$$

Hereafter we call the Lindblad superoperator (9) the exact Lindblad superoperator. Generally, finding the exact Lindblad superoperator (9) analytically or even numerically is a very difficult problem because the exact Lindblad superoperator $\hat{L}_{\mathrm{ex}}[\hat{\bar{\rho}}_S(t)]$ includes the product of the transition operators $\hat{S}_{\Delta\omega_{\alpha ij}}$. Finding the transition superoperators $\hat{S}_{\Delta\omega_{\alpha ij}}$ [Eq. (10)] is a very cumbersome problem because it demands the solution of the eigenproblem for the unified Hamiltonian $\hat{H}_S$. At the same time, the complexity of this eigenproblem grows exponentially with the number of subsystems.

As an alternative, we develop a perturbation approach for the analytical determination of the Lindblad superoperators. For future derivations, we introduce the operators

$$\hat{S}_{\alpha ij}^{(\mathrm{is})} = \langle k_{\alpha i}^{(\mathrm{is})}|\hat{S}_\alpha|k_{\alpha j}^{(\mathrm{is})}\rangle |k_{\alpha i}^{(\mathrm{is})}\rangle\langle k_{\alpha j}^{(\mathrm{is})}|. \qquad (12)$$

We assume that there is only pair interaction between subsystems (which is true for the vast majority of problems in quantum optics [49]) such that the interaction Hamiltonian $\hat{W}$ between subsystems has the form

$$\hat{W} = \hbar \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2} \hat{S}_{\alpha_1 i_1 j_1}^{(\mathrm{is})} \hat{S}_{\alpha_2 i_2 j_2}^{(\mathrm{is})}. \qquad (13)$$

For the simpler and clearer presentation we assume that the interaction between the subsystems (13) is defined by the same operators that introduce each system-environment interaction in Eq. (2). This assumption is true for the most optical systems. For example, the interactions of each two-level system (TLS) with dissipative and dephasing reservoirs are $\sim \sum_k (\hat{\sigma}_{1,2}^\dagger \hat{b}_k + \hat{b}_k^\dagger \hat{\sigma}_{1,2})$ and $\sim \sum_k \hat{\sigma}_{1,2}^\dagger \hat{\sigma}_{1,2}(\hat{b}_k + \hat{b}_k^\dagger)$, respectively ($\sigma_{1,2}$ and $\sigma_{1,2}^\dagger$ are lowering and raising operators between TLS states and $\hat{b}_k$ and $\hat{b}_k^\dagger$ are annihilation and creation operators of kth reservoir mode, respectively). At the same

time, the near-field interaction between dipole moments of two TLSs, which is the strongest electromagnetic interaction between subsystems at the nanoscale, is $\sim (\hat{\sigma}_1^\dagger \hat{\sigma}_2 + \hat{\sigma}_2^\dagger \hat{\sigma}_1)$, i.e., can be presented in the form (13). In Appendix A we discuss the extension of the theory developed for the general case.

To develop the perturbation approach for determination of the Lindblad superoperators we represent the Hamiltonian $\hat{\bar{H}}_{SR\alpha}(t)$ [Eq. (6)] as

$$\hat{\bar{H}}_{SR\alpha}(t) = \hbar\lambda_\alpha \sum_{ij} \hat{\mathbf{S}}_{\alpha ij}(t)\hat{R}_\alpha(t). \qquad (14)$$

In Eq. (14) we introduce the operators $\hat{R}_\alpha(t) = \exp(i\hat{H}_R t/\hbar)\hat{R}_\alpha \exp(-i\hat{H}_R t/\hbar)$ and $\hat{\mathbf{S}}_{\alpha ij}(t) = \exp(i\hat{H}_S t/\hbar)\hat{S}_{\alpha ij}^{(\mathrm{is})} \exp(-i\hat{H}_S t/\hbar)$, with $\hat{S}_{\alpha ij}^{(\mathrm{is})}$ defined by Eq. (12), and we use the fact that the eigenvectors $|k_{\alpha i}^{(\mathrm{is})}\rangle$ of the Hamiltonian $\hat{H}_S^{(\mathrm{is})}$ of isolated subsystems form the complete basis. The perturbation theory for determination of the Lindblad superoperators developed here is based on searching for the approximate expansion for the operators $\hat{\mathbf{S}}_{\alpha ij}(t) = \exp(i\hat{H}_S t/\hbar)\hat{S}_{\alpha ij}^{(\mathrm{is})} \exp(-i\hat{H}_S t/\hbar)$ in the form

$$\hat{\mathbf{S}}_{\alpha ij}(t) = \sum_n \varepsilon^n \hat{\mathbf{S}}_{\alpha ij}^{(n)}(t). \qquad (15)$$

To construct the Lindblad equation it is necessary to represent the operator $\hat{\mathbf{S}}_{\alpha ij}^{(n)}(t)$ in the form $\sum_{\Delta\omega^{(n)}} \hat{\mathbf{S}}_{\Delta\omega^{(n)}}^{(n)} \exp(-i\Delta\omega^{(n)}t)$, where the operators $\hat{\mathbf{S}}_{\Delta\omega^{(n)}}^{(n)}$ do not depend on time and $\Delta\omega^{(n)}$ are some yet unknown frequencies. Once such a representation is found, by applying the standard procedure we can arrive at the series expansion of the Lindblad superoperator

$$\hat{L}[\hat{\bar{\rho}}_S(t)] = \sum_{n=0}^{+\infty} \varepsilon^n \hat{L}^{(n)}[\hat{\bar{\rho}}_S(t)]. \qquad (16)$$

To find the coefficients $\hat{\mathbf{S}}_{\Delta\omega^{(n)}}^{(n)}$ and frequencies $\Delta\omega^{(n)}$, we solve the Heisenberg equation for $\hat{\mathbf{S}}_{\alpha ij}(t)$:

$$\frac{d\hat{\mathbf{S}}_{\alpha ij}(t)}{dt} = \frac{i}{\hbar}[\hat{H}_S, \hat{\mathbf{S}}_{\alpha ij}(t)]. \qquad (17)$$

The initial condition for Eq. (17) follows from the definition of $\hat{\mathbf{S}}_{\alpha ij}(t)$:

$$\hat{\mathbf{S}}_{\alpha ij}(0) = \hat{S}_{\alpha ij}^{(\mathrm{is})}. \qquad (18)$$

We solve Eq. (17) using the perturbation method with the small parameter ε. To do this we expand the operator $\hat{\mathbf{S}}_{\alpha ij}(t)$ in a power series of ε [Eq. (15)]. We substitute this series into Eq. (17) and collect all the terms with the same order of ε. As a result, the terms proportional to the zeroth order of ε give the equation for the zeroth order of the perturbation theory (see Appendix A),

$$\frac{d\hat{\mathbf{S}}_{\alpha ij}^{(0)}(t)}{dt} = -i\Delta\omega_{\alpha ij}^{(\mathrm{is})}\hat{\mathbf{S}}_{\alpha ij}^{(0)}(t), \qquad (19)$$

where $\Delta\omega_{\alpha ij}^{(\mathrm{is})} = \omega_{\alpha j}^{(\mathrm{is})} - \omega_{\alpha i}^{(\mathrm{is})}$. We obtain the initial condition for Eq. (19) from Eq. (18):

$$\hat{\mathbf{S}}_{\alpha ij}^{(0)}(0) = \hat{S}_{\alpha ij}^{(\mathrm{is})}. \qquad (20)$$

The solution to Eq. (19) with the initial condition (20) is

$$\hat{\mathbf{S}}^{(0)}_{\alpha ij}(t) = \hat{S}^{(is)}_{\alpha ij} \exp\left(-i\Delta\omega^{(is)}_{\alpha ij} t \right).\tag{21}$$

The direct application of the standard procedure for $\hat{\mathbf{S}}_{\alpha ij}(t) \approx \hat{\mathbf{S}}^{(0)}_{\alpha ij}(t)$ leads to the Lindblad superoperator

$$\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] = \sum_\alpha \sum_{ij} \lambda_\alpha^2 G_\alpha\big(\Delta\omega^{(is)}_{\alpha ij}\big) \big\{ \big[\hat{S}^{(0)}_{\alpha ij}, \hat{\tilde{\rho}}_S(t)\hat{S}^{(0)\dagger}_{\alpha ij}\big]$$
$$+ \big[\hat{S}^{(0)}_{\alpha ij}\hat{\tilde{\rho}}_S(t), \hat{S}^{(0)\dagger}_{\alpha ij}\big]\big\},\tag{22}$$

where $\hat{S}^{(0)}_{\alpha ij} = \hat{S}^{(is)}_{\alpha ij}$ and $\lambda_\alpha^2 G_\alpha(\Delta\omega^{(is)}_{\alpha ij})$ is defined by (11). We call the Lindblad superoperator (22) the Lindblad superoperator of the zeroth order of the perturbation theory, or in short

the zeroth-order Lindblad superoperator. Using the Lindblad superoperator (22), we can write the LGKS equation for the density matrix of the system $\hat{\tilde{\rho}}_S(t)$,

$$\frac{d\hat{\tilde{\rho}}_S(t)}{dt} = \hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)].\tag{23}$$

It can be seen from Eqs. (22) and (9) that the Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)]$ coincides with the one obtained with the standard procedure for the isolated subsystems in the absence of the interaction between the subsystems ($\varepsilon = 0$).

The first order of the perturbation theory for Eq. (17) may be obtained by the substitution of the series $\hat{\mathbf{S}}_{\alpha ij}(t) = \sum_n \varepsilon^n \hat{\mathbf{S}}^{(n)}_{\alpha ij}(t)$ into Eq. (17) and selecting the terms that are proportional to ε. As a result, we obtain the equation for $\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t)$ (see Appendix A),

$$\frac{d\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t)}{dt} = -i\Delta\omega^{(is)}_{\alpha ij}\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t) + i\left[\sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} w_{\alpha_1\alpha_2 i_1 j_1 i_2 j_2} \hat{\mathbf{S}}^{(0)}_{\alpha_1 i_1 j_1}(t)\hat{\mathbf{S}}^{(0)}_{\alpha_2 i_2 j_2}(t), \hat{\mathbf{S}}^{(0)}_{\alpha ij}(t) \right].\tag{24}$$

The initial condition for Eq. (24) follows from the initial condition (18) for the operator $\hat{\mathbf{S}}_{\alpha ij}(t)$ and takes the form

$$\hat{\mathbf{S}}^{(1)}_{\alpha ij}(0) = 0.\tag{25}$$

The solution of Eq. (24) with the initial condition (25) is (see Appendix A)

$$\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t) = \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} \frac{w_{\alpha_1\alpha_2 i_1 j_1 i_2 j_2}\big[\hat{S}^{(0)}_{\alpha_1 i_1 j_1}\hat{S}^{(0)}_{\alpha_2 i_2 j_2}, \hat{S}^{(0)}_{\alpha ij}\big]}{\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}} \big\{1 - \exp\big[-i\big(\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}\big)t\big]\big\} \exp\big(-i\Delta\omega^{(is)}_{\alpha ij}t\big).\tag{26}$$

Combining the solutions (21) and (26), we obtain the solution to Eq. (17) up to the first order of the perturbation theory $\hat{\mathbf{S}}_{\alpha ij}(t) \approx \hat{\mathbf{S}}^{(0)}_{\alpha ij}(t) + \varepsilon\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t)$,

$$\hat{\mathbf{S}}_{\alpha ij}(t) \approx \big(\hat{S}^{(0)}_{\alpha ij} + \varepsilon\hat{S}^{(1)}_{\alpha ij}\big)\exp\big(-i\Delta\omega^{(is)}_{\alpha ij}t\big) - \varepsilon\sum_{\alpha_1 \neq \alpha_2}\sum_{i_1 j_1 i_2 j_2} \frac{w_{\alpha_1\alpha_2 i_1 j_1 i_2 j_2}\big[\hat{S}^{(0)}_{\alpha_1 i_1 j_1}\hat{S}^{(0)}_{\alpha_2 i_2 j_2}, \hat{S}^{(0)}_{\alpha ij}\big]}{\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}}$$
$$\times \exp\big[-i\big(\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2} + \Delta\omega^{(is)}_{\alpha ij}\big)t\big],\tag{27}$$

where

$$\hat{S}^{(1)}_{\alpha ij} = \sum_{\alpha_1 \neq \alpha_2}\sum_{i_1 j_1 i_2 j_2} \frac{w_{\alpha_1\alpha_2 i_1 j_1 i_2 j_2}\big[\hat{S}^{(0)}_{\alpha_1 i_1 j_1}\hat{S}^{(0)}_{\alpha_2 i_2 j_2}, \hat{S}^{(0)}_{\alpha ij}\big]}{\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}}.\tag{28}$$

The direct application of the standard procedure for the operator $\hat{\mathbf{S}}_{\alpha ij}(t) \approx \hat{\mathbf{S}}^{(0)}_{\alpha ij}(t) + \varepsilon\hat{\mathbf{S}}^{(1)}_{\alpha ij}(t)$ leads to the Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$, with $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)]$ defined by Eq. (22) and $\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$ equal to

$$\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)] = \sum_\alpha \sum_{ij} \lambda_\alpha^2 G_\alpha\big(\Delta\omega^{(is)}_{\alpha ij}\big)\big\{\big[\hat{S}^{(1)}_{\alpha ij}, \hat{\tilde{\rho}}_S(t)\hat{S}^{(0)\dagger}_{\alpha ij}\big]$$
$$+ \big[\hat{S}^{(1)}_{\alpha ij}\hat{\tilde{\rho}}_S(t), \hat{S}^{(0)\dagger}_{\alpha ij}\big]\big\} + \sum_\alpha\sum_{ij}\lambda_\alpha^2 G_\alpha\big(\Delta\omega^{(is)}_{\alpha ij}\big)$$
$$\times \big\{\big[\hat{S}^{(0)}_{\alpha ij}, \hat{\tilde{\rho}}_S(t)\hat{S}^{(1)\dagger}_{\alpha ij}\big] + \big[\hat{S}^{(0)}_{\alpha ij}\hat{\tilde{\rho}}_S(t), \hat{S}^{(1)\dagger}_{\alpha ij}\big]\big\}.\tag{29}$$

We call the Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$ the Lindblad superoperator of the first order of the perturbation theory, or in short the first-order Lindblad

superoperator. Using the Lindblad superoperator (29), we can write the LGKS equation for the density matrix of the system as follows:

$$\frac{d\hat{\tilde{\rho}}_S(t)}{dt} = \hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)].\tag{30}$$

It is important to note that the Lindblad superoperator of the first order of the perturbation theory $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$ is nontrivial in the sense that, unlike the Lindblad superoperator (22), it cannot be represented as a sum of the Lindblad superoperators of isolated subsystems. Nevertheless, the Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$ is constructed from the product of the transition operators of the subsystems $\hat{S}^{(0)}_{\alpha ij}$ that can be seen from (28) and (29). Together, these two facts indicate that the first-order Lindblad superoperators of the perturbation theory takes into account the cross relaxation of the subsystems.

For practical applications it is more convenient to write the LGKS equation for the density matrix $\hat{\rho}_S(t)$ rather than for the density matrix in the interaction representation $\hat{\tilde{\rho}}_S(t)$. These two density matrices for the unified system are connected by

the equation that follows from Eq. (4):

$$\hat{\tilde{\rho}}_S(t) = \exp\left(i\frac{\hat{H}_S}{\hbar}t\right)\hat{\rho}_S(t)\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right). \qquad (31)$$

This transition from the density matrix $\hat{\tilde{\rho}}_S(t)$ to the density matrix $\hat{\rho}_S(t)$ in the LGKS equation (7) can be easily done because

$$\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\hat{L}_{\text{ex}}[\hat{\tilde{\rho}}_S(t)]\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) = \hat{L}_{\text{ex}}[\hat{\rho}_S(t)], \quad (32)$$

which follows from the definitions of the exact Lindblad superoperator $\hat{L}_{\text{ex}}[\hat{\tilde{\rho}}_S(t)]$ [see Eq. (9)] and the transition operators $\hat{S}_{\Delta\omega_{\alpha ij}}$ [see Eq. (10)]. As a result, the LGKS equation with the exact Lindblad superoperator for the density matrix $\hat{\rho}_S(t)$ takes the form

$$\frac{d\hat{\rho}_S(t)}{dt} = \frac{i}{\hbar}[\hat{\rho}_S(t), \hat{H}_S] + \hat{L}_{\text{ex}}[\hat{\rho}_S(t)]. \qquad (33)$$

The same transition can be done in the LGKS equations (23) and (30) with the zeroth-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)]$ and the first-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]$. To do this transition we use the approximate equalities

$$\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)]\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) \approx \hat{L}^{(0)}[\hat{\rho}_S(t)], \quad (34)$$

$$\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\{\hat{L}^{(0)}[\hat{\tilde{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\tilde{\rho}}_S(t)]\}\exp\left(i\frac{\hat{H}_S}{\hbar}t\right)$$
$$\approx \hat{L}^{(0)}[\hat{\rho}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\rho}_S(t)]. \qquad (35)$$

The difference between the left-hand side and the right-hand side of the approximate equality (34) is proportional to ε, which follows directly from Eq. (22) and initial condition (20) (see Appendix B). The difference between the left-hand side and the right-hand side of the approximate equality (35) is proportional to ε^2, which follows directly from Eqs. (29) and (27) (see Appendix B). Therefore, we can omit these terms on the right-hand sides of Eqs. (34) and (35). As a result, we obtain the LGKS equation for the density matrix $\hat{\rho}_S(t)$ with the zeroth-order Lindblad superoperator

$$\frac{d\hat{\rho}_S(t)}{dt} = \frac{i}{\hbar}[\hat{\rho}_S(t), \hat{H}_S] + \hat{L}^{(0)}[\hat{\rho}_S(t)] \qquad (36)$$

and the LGKS equation for the density matrix $\hat{\rho}_S(t)$ with the first-order Lindblad superoperator

$$\frac{d\hat{\rho}_S(t)}{dt} = \frac{i}{\hbar}[\hat{\rho}_S(t), \hat{H}_S] + \hat{L}^{(0)}[\hat{\rho}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\rho}_S(t)]. \quad (37)$$

We note that the LGKS equation (36) is equal to one used in the local approach [17–20]. Indeed, the Hamiltonian of the unified system, $\hat{H}_S = \hat{H}_S^{(\text{is})} + \varepsilon\hat{W}$, contains the interaction between the subsystems $\varepsilon\hat{W}$. At the same time the Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ coincides with the one obtained with the exact standard procedure, as it would be in the absence of the interaction between the subsystems,

$$\hat{L}^{(0)}[\hat{\rho}_S(t)] = \sum_{\text{subsystem}}\hat{L}_{\text{subsystem}}[\hat{\rho}_S(t)]. \qquad (38)$$

The relaxation dynamics, described by the LGKS equation (23), may violate the second law of thermodynamics and incorrectly predicts the dynamics of the system [20,33].

In the next section we show that although the Lindblad superoperator of the lower orders of the perturbation theory may violate the second law of thermodynamics, the Lindblad superoperator of the higher order of the perturbation theory restores the fulfillment of the second law of thermodynamics.

III. FULFILLMENT OF THE SECOND LAW OF THERMODYNAMICS

Below, for simplicity, we consider all the reservoirs to have zero temperature $T_\alpha = 0$, which is a good approximation for quantum optics. In this limit, the second law of the thermodynamics is equivalent to the demand that the energy flow between the system and reservoir is directed from the system to the reservoir. The energy flow in our case (when the Hamiltonian of the unified system $\hat{H}_S$ does not depend on time) is

$$J = \text{Tr}\left(\hat{H}_S\frac{d\hat{\rho}_S(t)}{dt}\right). \qquad (39)$$

The positive sign of the energy flow J indicates that the energy flows from the reservoir to the system. The negative sign of the energy flow J indicates that the energy flows from the system to the reservoir. Therefore, the second law of thermodynamics at zero temperature takes the form

$$J \leqslant 0. \qquad (40)$$

It is worth emphasizing that if there is no interaction between subsystems then, as was pointed out after Eq. (37), the LGKS equation (33) with the exact Lindblad superoperator takes the form

$$\frac{d\hat{\rho}_S(t)}{dt} = \frac{i}{\hbar}[\hat{\rho}_S(t), \hat{H}_S^{(\text{is})}] + \hat{L}^{(0)}[\hat{\rho}_S(t)]. \qquad (41)$$

This means that in the case of $\varepsilon = 0$ the Hamiltonian of the unified system is $\hat{H}_S = \hat{H}_S^{(\text{is})}$ and the exact Lindblad superoperator $\hat{L}_{\text{ex}}[\hat{\rho}_S(t)]$ is equal to the zeroth-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$. In this case, at zero temperature it is easy to prove that the second law of thermodynamics holds. Indeed, the substitution of Eq. (41) and the equality $\hat{H}_S = \hat{H}_S^{(\text{is})}$ into Eq. (39) and the use of the commutation relation $[\hat{H}_{\alpha S}^{(\text{is})}, \hat{S}_{\alpha ij}^{(0)}] = -\hbar\Delta\omega_{\alpha ij}^{(\text{is})}\hat{S}_{\alpha ij}^{(0)}$ leads to

$$J_0 = -2\hbar\sum_\alpha\sum_{\Delta\omega_{\alpha ij}\geqslant 0}\Delta\omega_{\alpha ij}^{(\text{is})}\lambda_\alpha^2 G_\alpha(\Delta\omega_{\alpha ij}^{(\text{is})})$$
$$\times \text{Tr}[\hat{S}_{\alpha ij}^{(0)\dagger}\hat{S}_{\alpha ij}^{(0)}\hat{\rho}_S(t)] \leqslant 0. \qquad (42)$$

In Eq. (42) the subscript 0 in J_0 means that the energy flow (39) is calculated when there is no interaction between subsystems ($\varepsilon = 0$). The definitions of $\Delta\omega_{\alpha ij}^{(0)}$ and $\hat{S}_{\alpha ij}^{(0)}$ are given after Eq. (22). The sum in Eq. (42) includes only nonnegative frequencies $\Delta\omega_{\alpha ij}^{(\text{is})}$ because at zero temperature and negative $\Delta\omega_{\alpha ij}^{(\text{is})}$, $G_\alpha(\Delta\omega_{\alpha ij}^{(\text{is})})$ is equal to zero (this means that only transitions with the energy flowing out of the system are possible) [17]. Thus, in this case the second law of thermodynamics holds (for a rigorous proof of the second law for arbitrary temperature see [18,19,46]).

When the subsystems interact with each other, it turns out that in the lower order of perturbation theory the second law of thermodynamics may be violated, whereas the higher order of the perturbation theory restores its fulfillment. Indeed, let us consider the zeroth order of perturbation theory. To obtain the energy flow between the unified system and the reservoirs, one should substitute Eq. (36) into Eq. (39). As a result we obtain (local approach)

$$J^{(0)} = \text{Tr}\{(\hat{H}_S^{(\text{is})} + \varepsilon \hat{W})\hat{L}^{(0)}[\hat{\rho}_S(t)]\} = J_0 + \varepsilon \Delta J_0, \quad (43)$$

where the (0) in $J^{(0)}$ means that the energy flow (39) is calculated with the zeroth-order Lindblad superoperator. The energy flow J_0 on the right-hand side of Eq. (43) is defined by Eq. (42). The energy flow ΔJ_0 on the right-hand side of Eq. (43) is

$$\Delta J_0 = \text{Tr}\{\hat{W}\hat{L}^{(0)}[\hat{\rho}_S(t)]\}. \quad (44)$$

As mentioned in the preceding section, the zeroth-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ does not take into account the cross-relaxation processes between the subsystems. This means that the application of the zeroth-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ leads to the additional "wrong" term $\varepsilon \Delta J_0$ in the energy flow (43) between the system and reservoirs. We showed after Eq. (42) that the term J_0, is nonpositive, but the wrong term $\varepsilon \Delta J_0$ may have a positive or a negative sign. As a result, when $\varepsilon \Delta J_0 > 0$ and $|J_0| < \varepsilon \Delta J_0$ the second law of thermodynamics is violated, because the energy starts to flow from the reservoir to the system, and $J^{(0)} > 0$.

Let us discuss how to determine the lowest order of the perturbation series that ensures the fulfillment of the second law of thermodynamics. To be more concrete, we consider two types of reservoirs: a dephasing reservoirs that does not change the energies of the isolated subsystems but affects the phases of the nondiagonal elements of the each of the subsystem density matrices and a dissipative reservoirs that drains the energy from the isolated subsystems. For example, the reservoir $\hat{R}$ interacting with a two-level system described by the Hamiltonian $\hat{H}_S^{(\text{is})} = \hbar \omega_{\text{TLS}} \hat{\sigma}^\dagger \hat{\sigma}$ (where the operator $\hat{\sigma} = |g\rangle\langle e|$ is the transition operator between the ground $|e\rangle$ and the excited $|g\rangle$ states of the TLS), through the coupling

Hamiltonian $\hat{H}_{SR}^{\text{deph}} = \hat{\sigma}^\dagger \hat{\sigma} \hat{R}_{\text{deph}}$, is dephasing. A reservoir which interacts with a TLS through the Hamiltonian $\hat{H}_{SR}^{\text{dis}} = (\hat{\sigma}^\dagger + \hat{\sigma})\hat{R}_{\text{dis}}$ is dissipative. Indeed, the Hamiltonian $\hat{H}_{SR}^{\text{deph}} = \hat{\sigma}^\dagger \hat{\sigma} \hat{R}_{\text{deph}}$ commutes with the TLS Hamiltonian $\hat{H}_S^{(\text{is})} = \hbar \omega_{\text{TLS}} \hat{\sigma}^\dagger \hat{\sigma}$, while the Hamiltonian $\hat{H}_{SR}^{\text{dis}} = (\hat{\sigma}^\dagger + \hat{\sigma})\hat{R}_{\text{dis}}$ does not.

When the interaction of an isolated subsystem with a dissipative reservoir permits transitions between system states and at least some $\Delta \omega_{\alpha ij}^{(\text{is})} \neq 0$, then according to Eq. (8), $J_0 < 0$, and the second law of thermodynamics holds until $\varepsilon |\Delta J_0| \leqslant |J_0|$. This puts a limit on the perturbation parameter. In this case, even using local Lindblad superoperators does not cause a violation of the second law of thermodynamics.

The situation changes when a subsystem interacts only with a dephasing reservoir [20,33]. In this case, all the frequencies $\Delta \omega_{\alpha ij}^{(\text{is})} = 0$ and consequently J_0 is equal to zero [see Eq. (42)]. Then the second law of thermodynamics in zeroth order (local approach) holds only if $\varepsilon = 0$ or $\varepsilon \Delta J_0 < 0$. In a general case, $\varepsilon \Delta J_0$ may be positive and the second law of thermodynamics would be violated. The addition of a dissipative reservoir may not help because now we require that $\varepsilon |\Delta J_0^{\text{deph}} + \Delta J_0^{\text{dis}}| \leqslant |J_0^{\text{dis}}|$. Thus, if the subsystems interact with each other, $\varepsilon \neq 0$, the local Lindblad superoperator, which does not take into account the cross-relaxation processes, may lead to a violation of the second law of thermodynamics [20,33] even if the system interacts with both dephasing and dissipative reservoirs. For example, the local Lindblad superoperator may lead to the pumping of the system by the dephasing reservoir with zero temperature [20,33].

Application of the first-order Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)] + \varepsilon \hat{L}^{(1)}[\hat{\rho}_S(t)]$ may fix this problem. Indeed, the substitution of Eq. (37) into the energy flow (39) gives the energy flow $J^{(1)}$ calculated with the zeroth-order Lindblad superoperator

$$\begin{aligned} J^{(1)} &= \text{Tr}\big((\hat{H}_S^{(\text{is})} + \varepsilon \hat{W})\{\hat{L}^{(0)}[\hat{\rho}_S(t)] + \varepsilon \hat{L}^{(1)}[\hat{\rho}_S(t)]\}\big) \\ &= J_1 + \varepsilon^2 \Delta J_1, \end{aligned} \quad (45)$$

where we introduce the energy flows

$$J_1 = -2\hbar \sum_\alpha \sum_{\Delta \omega_{\alpha ij} \geqslant 0} \Delta \omega_{\alpha ij}^{(\text{is})} \lambda_\alpha^2 G_\alpha(\Delta \omega_{\alpha ij}^{(\text{is})}) \text{Tr}\big[(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)})^\dagger (\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)})\hat{\rho}_S(t)\big], \quad (46)$$

$$\begin{aligned} \Delta J_1 &= 2\hbar \sum_\alpha \sum_{\Delta \omega_{\alpha ij} \geqslant 0} \Delta \omega_{\alpha ij}^{(\text{is})} \lambda_\alpha^2 G_\alpha(\Delta \omega_{\alpha ij}^{(\text{is})}) \text{Tr}\big[\hat{S}_{\alpha ij}^{(1)\dagger} \hat{S}_{\alpha ij}^{(1)} \hat{\rho}_S(t)\big] - 2\hbar \sum_\alpha \sum_{\Delta \omega_{\alpha ij} \geqslant 0} \Delta \omega_{\alpha ij}^{(\text{is})} \lambda_\alpha^2 G_\alpha(\Delta \omega_{\alpha ij}^{(\text{is})}) \text{Tr}\big\{\hat{S}_{\alpha ij}^{(0)\dagger}[\hat{W}, \hat{S}_{\alpha ij}^{(1)}]\hat{\rho}_S(t) \\ &\quad + [\hat{S}_{\alpha ij}^{(0)\dagger}, \hat{W}]\hat{S}_{\alpha ij}^{(1)}\hat{\rho}_S(t)\big\} - 2\hbar \sum_\alpha \sum_{\Delta \omega_{\alpha ij} \geqslant 0} \Delta \omega_{\alpha ij}^{(\text{is})} \lambda_\alpha^2 G_\alpha(\Delta \omega_{\alpha ij}^{(\text{is})}) \text{Tr}\big\{\hat{S}_{\alpha ij}^{(1)\dagger}[\hat{W}, \hat{S}_{\alpha ij}^{(0)}]\hat{\rho}_S(t) + [\hat{S}_{\alpha ij}^{(1)\dagger}, \hat{W}]\hat{S}_{\alpha ij}^{(0)}\hat{\rho}_S(t)\big\}. \quad (47) \end{aligned}$$

In Eq. (12) the operator $(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)})^\dagger (\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)})$ and the density matrix $\hat{\rho}_S(t)$ are non-negative, so the energy flow J_1 is negative or zero. The wrong term $\varepsilon^2 \Delta J_1$ on the right-hand side of Eq. (45) may have an arbitrary sign. If $J_1 < 0$ [see Eq. (45)], then the second law of thermodynamics is not violated until $\varepsilon^2 |\Delta J_1| \leqslant |J_1|$. Comparing this inequality ($\varepsilon^2 |\Delta J_1| \leqslant |J_1|$) with one that we obtained

with the zeroth-order Lindblad superoperator ($\varepsilon |\Delta J_0| \leqslant |J_0|$), we conclude that the first order of the perturbation theory preserves the second law of thermodynamics in the wider range of parameters than the zeroth order of the perturbation theory.

In a general case the correct description of the energy flow $J^{(n)}$ in the nth order demands knowledge of the nth order of the

Lindblad superoperator $\hat{L}^{(n)}[\hat{\rho}_S(t)]$. In the previous example, this means that to obtain the correct energy flow in the first order of perturbation theory it is necessary to use the first-order Lindblad superoperator $\hat{L}^{(1)}[\hat{\rho}_S(t)]$. We also note that the nth order of the perturbation theory leads to the wrong term in the energy flow $J^{(n)}$ that is proportional to ε^{n+1}.

The higher orders of the perturbation theory expand the range of parameters for which the second law of thermodynamics holds, because the nth order of the perturbation theory for the Lindblad superoperator describes the energy flow correctly with a precision up to ε^{n+1}. As was pointed out above, when the system interacts with dissipative and dephasing reservoirs, the main reason for the violation of the second law of thermodynamics is the interaction of the system with the dephasing reservoir. The reason is that the dephasing reservoir gives zero energy flow at $\varepsilon = 0$ and may give the energy flow from the reservoir to the system for $\varepsilon \neq 0$ at lower orders of the perturbation theory. The energy flow to the dissipative reservoir may be estimated as $\gamma \mathrm{Tr}[\hat{H}_S \hat{\rho}_S(t)]$, where γ is the dissipation rate of the unperturbed system. In accordance with Eqs. (43) and (45), in the nth order of the perturbation theory, possible energy flow from the dephasing reservoir to the system may be estimated as $\varepsilon^{n+1} \Gamma \mathrm{Tr}[\hat{H}_S \hat{\rho}_S(t)]$, where Γ is the dephasing rate at $\varepsilon = 0$. The fulfillment of the second law of thermodynamics demands that the energy flow from the system to the dissipative reservoir is greater than the wrong energy flow from the dephasing reservoir to the system. Thus, the order of the perturbation theory n required for the second law of thermodynamic to hold can be estimated as

$$\varepsilon^{n+1} < \gamma/\Gamma. \tag{48}$$

Below, by using specific examples, we show that the criterion (48) not only ensures the fulfillment of the second law of thermodynamics, but also defines the minimal necessary order of the perturbation theory that guarantees the correct prediction of the dynamics of an open quantum system.

IV. EXAMPLE: THE LINDBLAD SUPEROPERATOR FOR N COUPLED TWO-LEVEL SYSTEMS

The local Lindblad superoperator, which, as was shown in the Sec. II, is equal to the zeroth-order Lindblad superoperator (36), is widely used for the description of interacting quantum dots [2], qubits [1], and molecules [24], because the local Lindblad superoperator is easy to obtain. As we discussed above, the main drawback of the local Lindblad superoperator is that it may lead to a violation of the second law of thermodynamics [20,33]. In such a case, the dynamics of an open quantum system may differ from the exact dynamics not only quantitatively but also qualitatively. In particular, the local Lindblad superoperator may give unphysical results. Below we consider the dynamics of several interacting TLSs and show when a description based on local Lindblad superoperator fails and how the higher orders of the perturbation theory developed for the Lindblad superoperator restore the correct dynamics of an open quantum system.

To develop the perturbation theory for N interacting TLSs, we use the Hamiltonian

$$\hat{H}_S = \sum_{j=1}^{N} \hbar\omega_j \hat{\sigma}_j^\dagger \hat{\sigma}_j + \sum_{j=1}^{N} \sum_{k \neq j}^{N} \hbar g_{jk} \hat{\sigma}_j^\dagger \hat{\sigma}_k, \tag{49}$$

where the coupling constants obey the relationship $g_{jk} = g_{kj}^*$ because the Hamiltonian $\hat{H}_S$ is Hermitian. We consider a non-resonant case $|\omega_j - \omega_k| \gg |g_{jk}|$. Then $\varepsilon = |g_{jk}|/|\omega_j - \omega_k|$ can be used as a small parameter. We discuss the degenerate case ($|\omega_j - \omega_k| \ll |g_{jk}|$) for the problem of quantum transport in Appendix C.

The Hamiltonian of the reservoirs has the form

$$\hat{H}_R = \sum_{j,n} \hbar\omega_{jn}^{(a)} \hat{a}_{jn}^\dagger \hat{a}_{jn} + \sum_{j,n} \hbar\omega_{jn}^{(b)} \hat{b}_{jn}^\dagger \hat{b}_{jn}, \tag{50}$$

where the annihilation operators $\hat{a}_{jn}$ and $\hat{b}_{jn}$ belong to dissipative and dephasing reservoirs, respectively. The interaction between the system and the reservoirs is described by the Hamiltonian

$$\hat{H}_{SR} = \sum_{j,n} \hbar v_{jn}(\hat{\sigma}_j^\dagger + \hat{\sigma}_j)(\hat{a}_{jn}^\dagger + \hat{a}_{jn})$$
$$+ \sum_{j,n} \hbar w_{jn} \hat{\sigma}_j^\dagger \hat{\sigma}_j(\hat{b}_{jn}^\dagger + \hat{b}_{jn}). \tag{51}$$

If we neglect an interaction between the TLSs ($g_{jk} = 0$), the Lindblad equation for the density matrix of the whole system $\hat{\rho}_S(t)$ can be easily obtained [16]

$$\frac{\partial}{\partial t} \hat{\rho}_S(t) = \frac{i}{\hbar}\left[\hat{\rho}_S(t), \hat{H}_S^{(0)}\right] + \hat{L}^{(0)}[\hat{\rho}_S(t)], \tag{52}$$

where

$$\hat{H}_S^{(0)} = \sum_{j=1}^{N} \hbar\omega_j \hat{\sigma}_j^\dagger \hat{\sigma}_j, \tag{53}$$

$$\hat{L}^{(0)}[\hat{\rho}_S] = \sum_{j=1}^{N} \gamma_j \bar{n}(-\omega_j)(2\hat{\sigma}_j \hat{\rho}_S \hat{\sigma}_j^\dagger - \hat{\sigma}_j^\dagger \hat{\sigma}_j \hat{\rho}_S - \hat{\rho}_S \hat{\sigma}_j^\dagger \hat{\sigma}_j)$$
$$+ \sum_{j=1}^{N} \gamma_j \bar{n}(\omega_j)(2\hat{\sigma}_j^\dagger \hat{\rho}_S \hat{\sigma}_j - \hat{\sigma}_j \hat{\sigma}_j^\dagger \hat{\rho}_S - \hat{\rho}_S \hat{\sigma}_j \hat{\sigma}_j^\dagger)$$
$$+ \sum_{j=1}^{N} \Gamma_j (2\hat{\sigma}_j^\dagger \hat{\sigma}_j \rho \hat{\sigma}_j^\dagger \hat{\sigma}_j - \hat{\sigma}_j^\dagger \hat{\sigma}_j \rho - \rho \hat{\sigma}_j^\dagger \hat{\sigma}_j), \tag{54}$$

$$\bar{n}(\omega) = \begin{cases} (\exp(\hbar\omega/T) - 1)^{-1}, & \omega > 0 \\ 1 + (\exp(\hbar|\omega|/T) - 1)^{-1}, & \omega < 0, \end{cases} \tag{55}$$

$$\gamma_j = \pi\hbar \sum_n |v_{jn}|^2 \delta(\omega_{jn}^{(a)} - \omega_j), \tag{56}$$

$$\Gamma_j = \pi\hbar \lim_{\omega \to 0} \sum_n |w_{jn}|^2 \delta(\omega_{jn}^{(a)} - \omega)[\bar{n}(\omega) - \bar{n}(-\omega)]. \tag{57}$$

Note that the dephasing rates Γ_j are mainly determined by the low-frequency behavior of the reservoirs.

As discussed in the preceding section, the master equation (52) preserves the second law of thermodynamics. When $g_{jk} \neq 0$, the zeroth-order term of the perturbation theory coincides with the local approach for the Lindblad superoperators and leads to the master equation

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) = \frac{i}{\hbar}[\hat{\rho}_S(t), \hat{H}_S] + \hat{L}^{(0)}[\hat{\rho}_S(t)], \qquad (58)$$

where $\hat{H}_S$ is defined by Eq. (49) and $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ is defined by Eq. (54).

In this case, the interaction between the TLSs is taken into account in the Hamiltonian $\hat{H}_S$ but not in the Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$. This superoperator describes the relaxation in the case of noninteracting TLSs [see Eq. (52)]. According to the discussion in the preceding section, it is not surprising that the master equation (58) may lead to a violation of the second law of the thermodynamics.

To obtain the Lindblad superoperators in the first order of the perturbation theory, one should solve the Heisenberg equation for $\hat{\sigma}_j(t)$,

$$d\hat{\sigma}_j(t)/dt = -i\omega_j\hat{\sigma}_j(t) + i[2\hat{\sigma}_j^\dagger(t)\hat{\sigma}_j(t) - 1]$$
$$\times \sum_{\substack{k=1 \\ k\neq j}}^N g_{jk}\hat{\sigma}_k(t), \quad \hat{\sigma}_j(0) = \hat{\sigma}_j. \qquad (59)$$

To solve Eq. (59), we expand the operator $\hat{\sigma}_j(t)$ into a series $\hat{\sigma}_j(t) = \hat{\sigma}_j^{(0)}(t) + \varepsilon\hat{\sigma}_j^{(1)}(t) + \cdots$ by using the perturbation theory with the small parameter $\varepsilon = |g_{jk}|/|\omega_j - \omega_k|$. The-zeroth order approximation $\hat{\sigma}_j^{(0)}(t)$ satisfies the equation

$$d\hat{\sigma}_j^{(0)}(t)/dt = -i\omega_j\hat{\sigma}_j^{(0)}(t), \quad \hat{\sigma}_j^{(0)}(0) = \hat{\sigma}_j, \qquad (60)$$

and has the form $\hat{\sigma}_j^{(0)}(t) = \hat{\sigma}_j \exp(-i\omega_j t)$.

The first-order approximation term $\hat{\sigma}_j^{(1)}(t)$ is governed by the equation

$$d\hat{\sigma}_j^{(1)}(t)/dt = -i\omega_j\hat{\sigma}_j^{(1)}(t) + i[2\hat{\sigma}_j^{(0)\dagger}(t)\hat{\sigma}_j^{(0)}(t) - 1]$$
$$\times \sum_{\substack{k=1 \\ k\neq j}}^N g_{jk}\hat{\sigma}_k^{(0)}(t), \quad \hat{\sigma}_j^{(1)}(0) = 0. \qquad (61)$$

The solution to Eq. (61) is

$$\hat{\sigma}_j^{(1)}(t) = -(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}}{\omega_j - \omega_k}\hat{\sigma}_k \exp(-i\omega_j t)$$

$$+ (2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}}{\omega_j - \omega_k}\hat{\sigma}_k \exp(-i\omega_k t). \qquad (62)$$

Employing Eqs. (60) and (61), we can obtain the solution to Eq. (59) in the first order with respect to ε:

$$\hat{\sigma}_j(t) \approx \left(\hat{\sigma}_j - \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k}\right) \exp(-i\omega_j t)$$
$$+ \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k} \exp(-i\omega_k t). \qquad (63)$$

In the same order, from Eq. (63) one can obtain

$$\hat{\sigma}_j^\dagger\hat{\sigma}_j(t) \approx \left(\hat{\sigma}_j^\dagger\hat{\sigma}_j + \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{kj}\hat{\sigma}_j\hat{\sigma}_k^\dagger + g_{jk}\hat{\sigma}_j^\dagger\hat{\sigma}_k}{\omega_j - \omega_k}\right)$$
$$- \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{kj}\hat{\sigma}_j\hat{\sigma}_k^\dagger}{\omega_j - \omega_k} \exp[i(\omega_k - \omega_j)t]$$
$$+ \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{kj}\hat{\sigma}_k\hat{\sigma}_j^\dagger}{\omega_j - \omega_k} \exp[i(\omega_j - \omega_k)t]. \qquad (64)$$

Now we use approximate the expressions (63) and (64) for deriving the Lindblad superoperator in the first order. As a result, we obtain the master equation with the Lindblad superoperators in the first order of the perturbation theory

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S] + \hat{L}^{(0)}[\hat{\rho}_S(t)] + \hat{L}^{(1)}[\hat{\rho}_S(t)], \qquad (65)$$

where $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ is defined by Eq. (54) and

$$\hat{L}^{(1)}[\hat{\rho}_S(t)] = -\sum_{j=1}^N \gamma_j\bar{n}(-\omega_j)\left(\left[\hat{\sigma}_j, \hat{\rho}_S\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k^\dagger}{\omega_j - \omega_k}\right] + \left[\hat{\sigma}_j\hat{\rho}_S, \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k^\dagger}{\omega_j - \omega_k}\right]\right)$$

$$- \sum_{j=1}^N \gamma_j\bar{n}(-\omega_j)\left(\left[\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k}, \hat{\rho}_S\hat{\sigma}_j^\dagger\right] + \left[\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k}\hat{\rho}_S, \hat{\sigma}_j^\dagger\right]\right)$$

$$- \sum_{j=1}^N \gamma_j\bar{n}(\omega_j)\left(\left[\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k^\dagger}{\omega_j - \omega_k}, \hat{\rho}_S\hat{\sigma}_j\right] + \left[\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k^\dagger}{\omega_j - \omega_k}\hat{\rho}_S, \hat{\sigma}_j\right]\right)$$

$$+ \sum_{j=1}^N \gamma_j\bar{n}(\omega_j)\left(\left[\hat{\sigma}_j^\dagger, \hat{\rho}_S\sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k}\right] + \left[\hat{\sigma}_j^\dagger\hat{\rho}_S, \sum_{\substack{k=1 \\ k\neq j}}^N \frac{g_{jk}(2\hat{\sigma}_j^\dagger\hat{\sigma}_j - 1)\hat{\sigma}_k}{\omega_j - \omega_k}\right]\right)$$

$$+ \sum_{j=1}^{N} \Gamma_j \left(\left[\hat{\sigma}_j^\dagger \hat{\sigma}_j, \hat{\rho}_S \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{g_{kj} \hat{\sigma}_j \hat{\sigma}_k^\dagger + g_{jk} \hat{\sigma}_j^\dagger \hat{\sigma}_k}{\omega_j - \omega_k} \right] + \left[\hat{\sigma}_j^\dagger \hat{\sigma}_j \hat{\rho}_S, \sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{g_{kj} \hat{\sigma}_j \hat{\sigma}_k^\dagger + g_{jk} \hat{\sigma}_j^\dagger \hat{\sigma}_k}{\omega_j - \omega_k} \right] \right)$$

$$+ \sum_{j=1}^{N} \Gamma_j \left(\left[\sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{g_{kj} \hat{\sigma}_j \hat{\sigma}_k^\dagger + g_{jk} \hat{\sigma}_j^\dagger \hat{\sigma}_k}{\omega_j - \omega_k}, \hat{\rho}_S \hat{\sigma}_j^\dagger \hat{\sigma}_j \right] + \left[\sum_{\substack{k=1 \\ k \neq j}}^{N} \frac{g_{kj} \hat{\sigma}_j \hat{\sigma}_k^\dagger + g_{jk} \hat{\sigma}_j^\dagger \hat{\sigma}_k}{\omega_j - \omega_k} \hat{\rho}_S, \hat{\sigma}_j^\dagger \hat{\sigma}_j \right] \right). \tag{66}$$

Below, to illustrate how the theory works, we discuss examples with a minimum number of subsystems. For this purpose, we consider several complex open quantum systems and compare the dynamics predicted by the master equations with the following superoperators: (i) the exact Lindblad superoperators [see (33)], (ii) the Lindblad superoperators obtained by the perturbation theory, and (iii) the local Lindblad superoperators. As was discussed in Sec. II [see Eq. (9)], to obtain the exact Lindblad superoperators we use computer simulations to solve the eigenproblem for the Hamiltonian (49) and implement the standard procedure.

We start with a system containing two TLSs and having two different transition frequencies ω_1 and $\omega_2 = 1.2\omega_1$, dephasing rates $\Gamma_1 = 10^{-3}\omega_1$ and $\Gamma_2 = 10^{-3}\omega_1$, and dissipation rates $\gamma_1 = 10^{-7}\omega_1$ and $\gamma_2 = 10^{-6}\omega_1$. We assume that the temperature is zero $T = 0$ and the coupling constants are the same $g_{12} = g_{21} = g = 0.01\omega_1$. In this case $g \ll |\omega_2 - \omega_1|$. To emphasize the necessity of the perturbation approach, we consider the case when the dephasing rates are much greater than the dissipative rates $\Gamma_1, \Gamma_2 \gg \gamma_1, \gamma_2$. This relationship between the dephasing and the dissipative rates is typical for quantum dots [50–52] and dye molecules [53,54]. For certainty, we assume that initially the first TLS is in the excited state, while the second TLS is in the ground state. The time dependence of the system energy $E(t) = \text{Tr}[\hat{\rho}_S(t)\hat{H}_S]$ when calculated with the local approach (zeroth order of the perturbation theory) (58), the first-order master equation (65), and the exact master equation is shown in Fig. 1. One can see that the first-order perturbation theory is in good agreement with the solution of the exact Lindblad equation. However, not only does the local Lindblad equation give dynamics that differs from that given by the exact Lindblad equation, it also predicts that the energy of the system rises with time and becomes greater than the initial system energy (Fig. 1). This violates the second law of thermodynamics in the Clausius form [16,17] because this additional energy originates from the energy flow from the reservoir to the system at zero temperature. From Fig. 2 one can see that the local Lindblad equation predicts energy transfers from the low-energy TLS to the high-energy TLS in such a way that the total energy of the system rises. At the same time, both the first-order perturbation theory and the exact Lindblad equation show that this transition is suppressed (Fig. 2).

In this example, the criterion (48) is violated in the zeroth order of the perturbation theory for the Lindblad superoperator (the local approach) with the small parameter $\varepsilon = g/(\omega_2 - \omega_1)$. As expected, the local approach leads to a violation of the second law of thermodynamics. Indeed, the net energy flow is directed from the dephasing reservoir to the system and more

importantly this energy flow exceeds the energy flow from the system to the dissipative reservoirs (see Figs. 1 and 2).

At the same time, the first order of the perturbation theory satisfies the criterion (48) and, as Figs. 1 and 2 show, the total energy flow is directed from the system to the reservoirs. Therefore, the dynamics of the system predicted by the first order of the perturbation theory and by the exact Lindblad superoperators are in good agreement.

In the next example, we show how cross-relaxation processes affect the quantum transport through a chain of three TLSs with the frequencies ω_1, ω_2, and ω_3 such that $\omega_1 < \omega_2$, $\omega_3 < \omega_2$, and $\omega_1 < \omega_3$ (Fig. 3). The Hamiltonian of the system has the form (49) with the coupling constants $g_{13} = g_{31} = 0$ and $g_{12} = g_{23} = g_{21} = g_{32} = g \neq 0$:

$$\hat{H}_S = \hbar\omega_1 \hat{\sigma}_1^\dagger \hat{\sigma}_1 + \hbar\omega_2 \hat{\sigma}_2^\dagger \hat{\sigma}_2 + \hbar\omega_3 \hat{\sigma}_3^\dagger \hat{\sigma}_3 + \hbar g(\hat{\sigma}_1^\dagger \hat{\sigma}_2 + \hat{\sigma}_2^\dagger \hat{\sigma}_1)$$
$$+ \hbar g(\hat{\sigma}_2^\dagger \hat{\sigma}_3 + \hat{\sigma}_2^\dagger \hat{\sigma}_3). \tag{67}$$

Each of these TLSs interacts with dissipative and dephasing reservoirs, which have Hamiltonians (50). In the interaction Hamiltonians (51) j is equal to 1, 2, or 3 for the first, second, or third TLS, respectively. We assume that all the dissipation rates (56) are the same, $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$, and that the dephasing rates (57) are also identical, $\Gamma_1 = \Gamma_2 = \Gamma_3 = \Gamma$. In a quantum transport problem, it is common to
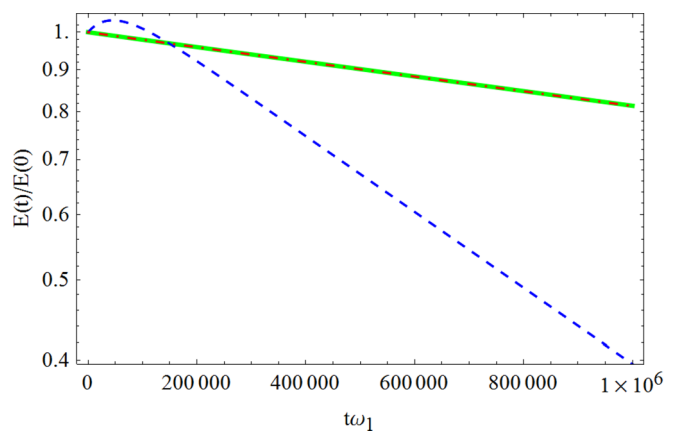

FIG. 1. System energy normalized by its initial energy. The parameters of the system are $\omega_2 = 1.2\omega_1$, $g = 0.01\omega_1$, $\Gamma_1 = \Gamma_2 = 10^{-3}\omega_1$, $\gamma_1 = 10^{-7}\omega_1$, $\gamma_2 = 10^{-6}\omega_1$, and temperature $T = 0$. Initially, the first and the second TLSs are in the excited and ground states, respectively. Blue dashed, red dash-dotted, and green solid lines are obtained by solving the local Lindblad equation, by using the perturbation theory, and by solving the exact Lindblad equation, respectively.
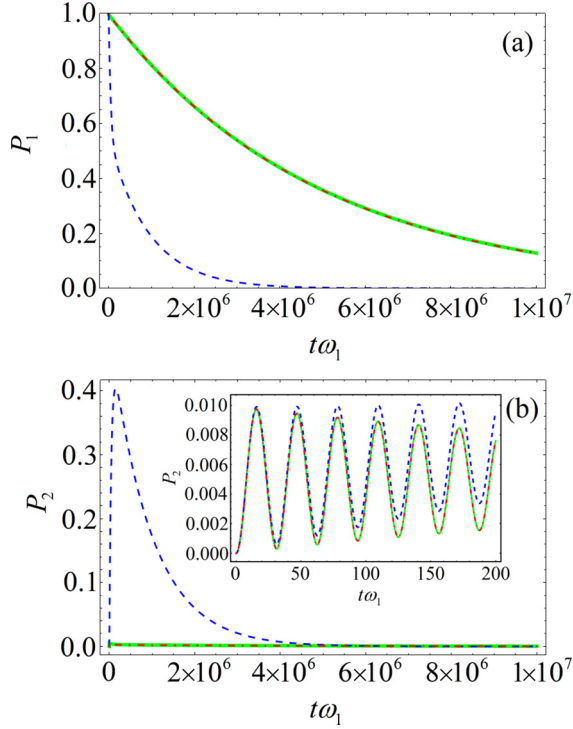
FIG. 2. Time dependence of the probability of (a) the first TLS and (b) the second TLS to be in the exited state. The inset shows the probability of the second TLS to be in the exited state at a smaller scale in time. The parameters and the lines are described in Fig. 1.

introduce an additional relaxation channel that drains excitations from the end of the TLS chain [30]. In our case, this is the third TLS, which has additional relaxation described by the Lindblad superoperator [30]

$$L_{\text{drain}}(\hat{\rho}_S) = \gamma_{\text{drain}}(2\hat{\sigma}_3\hat{\rho}_S\hat{\sigma}_3^\dagger - \hat{\sigma}_3^\dagger\hat{\sigma}_3\hat{\rho}_S - \hat{\rho}_S\hat{\sigma}_3^\dagger\hat{\sigma}_3). \quad (68)$$

We assume that the rate of the excitation drain γ_{drain} is faster than the dissipation rate of this TLS, $\gamma_{\text{drain}} \gg \gamma$.

Thus, the master equation for the density matrix of the system $\hat{\rho}_S$ takes the form

$$\frac{\partial}{\partial t}\hat{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}_S] + \hat{L}[\hat{\rho}_S(t)] + \hat{L}_{\text{drain}}[\hat{\rho}_S(t)], \quad (69)$$

where the Hamiltonian $\hat{H}_S$ and the Lindblad superoperator $\hat{L}_{\text{drain}}[\hat{\rho}_S(t)]$ are defined by Eqs. (67) and (68), respectively, and the Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$ that arises due to interactions of the TLSs with dissipating and dephasing reservoirs is described by Eqs. (50) and (51), respectively. Note that in the zeroth order of the perturbation theory, the
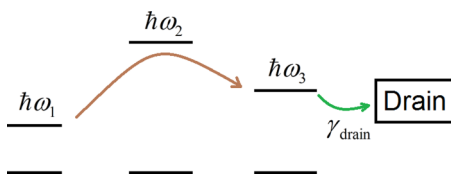

FIG. 3. Schematic of the TLS chain. At the initial moment, only the first TLS is excited.
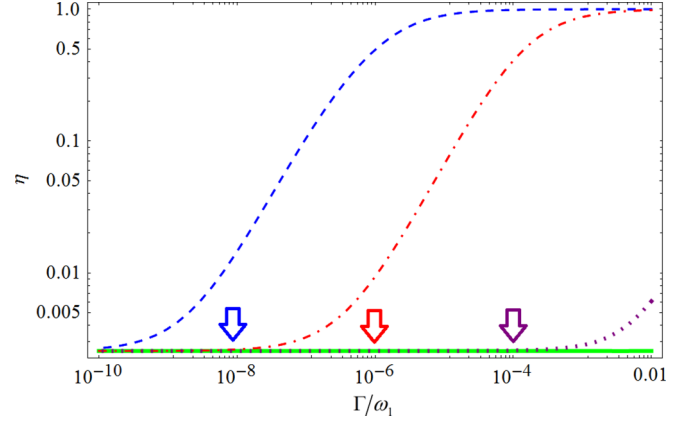
Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)]$ defined by Eq. (54) coincides with the Lindblad superoperator obtained with the local approach [2,21–32]. In the first order of the perturbation theory, the Lindblad superoperator takes the form $\hat{L}^{(0)}[\hat{\rho}_S(t)] + \hat{L}^{(1)}[\hat{\rho}_S(t)]$, where $\hat{L}^{(1)}[\hat{\rho}_S(t)]$ is defined by Eq. (66).

At the initial moment, only the first TLS is excited. The capability of the system to conduct the excitation from the first TLS to the third is characterized by the quantum transport efficiency η defined as [30]

$$\eta = -\int_0^{+\infty} \text{tr}[\hat{\sigma}_3^\dagger\hat{\sigma}_3 L_{\text{drain}}(\hat{\rho}_S)]dt. \quad (70)$$

From a physical point of view, the quantum transport efficiency η of the chain of the TLSs is the probability of the initial excitation of the first TLS to be transmitted to the drain.

The dependence of the quantum transport efficiency on the dephasing rate is shown in Fig. 4. The master equation (69) with the exact Lindblad superoperator $\hat{L}_{\text{ex}}[\hat{\rho}_S(t)]$ [Eq. (9)] predicts that the quantum transport efficiency η is very small and is independent of the dephasing rate Γ (the green solid line in Fig. 4).

As one can see from Fig. 4, the dynamics predicted with the local Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)] = \hat{L}^{(0)}[\hat{\rho}_S(t)]$ fails to describe the quantum transport when the dephasing rate Γ is greater than the value

$$\Gamma > \gamma(\omega_2 - \omega_1)/g. \quad (71)$$

The reason for this is that the local Lindblad equation does not include cross relaxations. It is important to note that the inequality (71) coincides with the criterion (48), which is

FIG. 4. Dependence of the quantum transport efficiency η on the dephasing rate Γ. The parameters of the system are $\omega_2 = 2\omega_1$, $g = 0.01\omega_1$, $\gamma = 10^{-10}\omega_1$, $\gamma_{\text{drain}} = 10^{-6}\omega_1$, and (a) $\omega_3 = 0.8\omega_1$ and (b) $\omega_3 = 1.2\omega_1$. The blue dashed line corresponds to master equation (69) with the local Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$, the red dash-dotted line corresponds to master equation (69) with the Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$ obtained in the first order of the perturbation theory, the purple dotted line corresponds to master equation (69) with the Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$ obtained in the second order of the perturbation theory, and the green solid line corresponds to master equation (69) with the exact Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$. Arrows indicate the dephasing rate Γ above which the criterion (48) is violated with $\varepsilon = g/|\omega_2 - \omega_1|$ and $n = 0$ (blue arrow), $n = 1$ (red arrow), and $n = 2$ (purple arrow).

needed for the second law of thermodynamics to hold. To compare Eqs. (71) and (48) we have to set $\varepsilon = g/|\omega_2 - \omega_1|$ and $n = 0$ in Eq. (48).

The master equation (69) with the Lindblad superoperator $\hat{L}^{(0)}[\hat{\rho}_S(t)] + \hat{L}^{(1)}[\hat{\rho}_S(t)]$ obtained in the first order of perturbation theory describes the cross relaxation of the neighboring TLSs. The quantum transport efficiency calculated with the perturbation theory is close to the one calculated with the exact Lindblad superoperators with a wide range of dephasing rates (Fig. 4). The first-order perturbation theory fails to describe the quantum transport efficiency when

$$\Gamma > \gamma[(\omega_2 - \omega_1)/g]^2. \tag{72}$$

The reason for this is that the first-order perturbation theory describes the cross relaxation only for the neighboring TLSs. However, at high dephasing rates, the main role of the quantum efficiency is played by the cross relaxation of the first and third TLSs. Note that the inequality (72) is in agreement with the criterion (48) for $n = 1$.

Now we consider the second order of the perturbation theory. As discussed at the beginning of this section, to obtain the Lindblad superoperator $\hat{L}[\hat{\rho}_S(t)]$ one should solve the Heisenberg equation (59) within the perturbation theory up to the second order of the small parameter $g/|\omega_2 - \omega_1|$. The derivation of this solution is long but straightforward. The result of the solution is

$$\hat{\sigma}_1(t) = \hat{\varsigma}_1 e^{-i\omega_1 t} + \frac{g}{\omega_1 - \omega_2}(2\hat{\varsigma}_1^\dagger \hat{\varsigma}_1 - 1)\hat{\varsigma}_2 e^{-i\omega_2 t} + \frac{g^2}{(\omega_1 - \omega_3)(\omega_2 - \omega_3)}(2\hat{\varsigma}_1^\dagger \hat{\varsigma}_1 - 1)(2\hat{\varsigma}_2^\dagger \hat{\varsigma}_2 - 1)\hat{\varsigma}_3 e^{-i\omega_3 t}, \tag{73}$$

$$\hat{\sigma}_2(t) = \hat{\varsigma}_2 e^{-i\omega_2 t} + (2\hat{\varsigma}_2^\dagger \hat{\varsigma}_2 - 1)\left(\frac{g}{\omega_2 - \omega_3}\hat{\varsigma}_3 e^{-i\omega_3 t} + \frac{g}{\omega_2 - \omega_1}\hat{\varsigma}_1 e^{-i\omega_1 t}\right) + 2\frac{g^2}{(\omega_1 - \omega_3)(\omega_2 - \omega_3)}\hat{\varsigma}_1 \hat{\varsigma}_2 \hat{\varsigma}_3^\dagger e^{-i(\omega_1 + \omega_2 - \omega_3)t}$$

$$+ 2\frac{g^2}{(\omega_3 - \omega_1)(\omega_2 - \omega_1)}\hat{\varsigma}_1^\dagger \hat{\varsigma}_2 \hat{\varsigma}_3 e^{-i(-\omega_1 + \omega_2 + \omega_3)t} + 2\frac{g}{\omega_1 + \omega_3 - 2\omega_2}\left(\frac{g}{\omega_2 - \omega_3} + \frac{g}{\omega_2 - \omega_1}\right)\hat{\varsigma}_1 \hat{\varsigma}_2^\dagger \hat{\varsigma}_3 e^{-i(\omega_1 - \omega_2 + \omega_3)t}, \tag{74}$$

$$\hat{\sigma}_3(t) = \hat{\varsigma}_3 e^{-i\omega_3 t} + \frac{g}{\omega_3 - \omega_2}(2\hat{\varsigma}_3^\dagger \hat{\varsigma}_3 - 1)\hat{\varsigma}_2 e^{-i\omega_2 t} + \frac{g^2}{(\omega_3 - \omega_1)(\omega_2 - \omega_1)}(2\hat{\varsigma}_3^\dagger \hat{\varsigma}_3 - 1)(2\hat{\varsigma}_2^\dagger \hat{\varsigma}_2 - 1)\hat{\varsigma}_1 e^{-i\omega_1 t}, \tag{75}$$

where the operators $\hat{\varsigma}_1$, $\hat{\varsigma}_2$, and $\hat{\varsigma}_3$ can be derived from the conditions $\hat{\sigma}_1(0) = \hat{\sigma}_1$, $\hat{\sigma}_2(0) = \hat{\sigma}_2$, and $\hat{\sigma}_3(0) = \hat{\sigma}_3$.

The master equation (69) with the Lindblad superoperator obtained in the second order of the perturbation theory predicts the quantum efficiency, which is in good agreement with the one calculated with the exact Lindblad superoperators in a wide range of the dephasing rate Γ (Fig. 4). The second order of the perturbation theory describes the cross correlations of all three TLSs but does not correctly predict the quantum transport efficiency when the dephasing rate Γ is as high as

$$\Gamma > \gamma[(\omega_2 - \omega_1)/g]^3. \tag{76}$$

The inequality (76) is the same as the criterion (48) for $n = 2$.

Thus, in the case of the TLS chain shown in Fig. 3, the transport efficiency cannot be significantly improved by increasing the dephasing rate of each TLS (Fig. 4). This contradicts the local theory that leads to incorrect system dynamics. The perturbation theory takes into account the cross-relaxation processes between TLSs and restores the correct dynamics of the system (Fig. 4). At the same time, the correct description of the system dynamics at higher dephasing rates requires higher orders of the perturbation theory.

V. CONCLUSION

In this paper we have analyzed the applicability of Lindblad superoperators obtained within the local theory to the problems of open quantum systems and developed a perturbation theory for the Lindblad superoperators for open quantum systems containing several interacting subsystems.

Each subsystem also interacts with its own reservoirs. When the local Lindblad superoperators are applied, the second law of thermodynamics may be violated and the prediction of the dynamics of the system may be incorrect. We have shown that the main reason for this is the interaction of the system with dephasing reservoirs. The perturbation theory that we developed can restore the correct dynamics of an open quantum system and provide the fulfillment of the second law of thermodynamics. The perturbation theory developed for the Lindblad superoperators can be applied to various open quantum system problems. The theory does not require additional complicated calculations, such as solving the eigenvalue problem, and it takes into account cross relaxation that may play an important role in the dynamics of an open quantum system.

APPENDIX A: PERTURBATION THEORY FOR TRANSITION OPERATORS

In this Appendix we present the details of the derivation of perturbation series for the Lindblad superoperator. We consider the system with the Hamiltonian (1).

First, we consider the case $\varepsilon = 0$ in the Hamiltonian (1), which corresponds to the separate subsystems, and discuss the well-known results. According to the well-known standard algorithm [19] for obtaining the Lindblad equation in the case

$\varepsilon = 0$, the Schrödinger operator $\hat{S}_\alpha$ should be expanded in the basis of the eigenstates $|k_{\alpha i}^{(is)}\rangle$ of the subsystem Hamiltonian $H_{S\alpha}^{(is)}$,

$$\hat{S}_\alpha = \sum_{ij \in \alpha} \langle k_{\alpha i}^{(is)} | \hat{S}_\alpha | k_{\alpha j}^{(is)} \rangle | k_{\alpha i}^{(is)} \rangle \langle k_{\alpha j}^{(is)} | = \sum_{ij} \hat{S}_{\alpha ij}^{(is)}, \quad (A1)$$

where

$$\hat{S}_{\alpha ij}^{(is)} = \langle k_{\alpha i}^{(is)} | \hat{S}_\alpha | k_{\alpha j}^{(is)} \rangle | k_{\alpha i}^{(is)} \rangle \langle k_{\alpha j}^{(is)} |, \quad \Delta\omega_{\alpha ij}^{(is)} = \omega_{\alpha j}^{(is)} - \omega_{\alpha i}^{(is)}. \quad (A2)$$

Since all the eigenstates $|k_{\alpha i}^{(is)}\rangle$ and the eigenfrequencies $\omega_{\alpha i}^{(is)}$ of the Hamiltonians $\hat{H}_{S\alpha}^{(is)}$ are assumed to be known, the interaction representation for the operators $\hat{S}_\alpha$ takes the form

$$\begin{aligned}
&\exp\left(i\hat{H}_S^{(is)} t/\hbar\right) \hat{S}_\alpha \exp\left(-i\hat{H}_S^{(is)} t/\hbar\right) \\
&= \exp(i\hat{H}_{S\alpha}^{(is)} t/\hbar) \hat{S}_\alpha \exp\left(-i\hat{H}_{S\alpha}^{(is)} t/\hbar\right) \\
&= \sum_{ij} \langle k_{\alpha i}^{(is)} | \hat{S}_\alpha | k_{\alpha j}^{(is)} \rangle | k_{\alpha i}^{(is)} \rangle \langle k_{\alpha j}^{(is)} | \exp\left(-i\Delta\omega_{\alpha ij}^{(is)} t\right) \\
&= \sum_{ij} \hat{S}_{\alpha ij}^{(is)} \exp\left(-i\Delta\omega_{\alpha ij}^{(is)} t\right), \quad (A3)
\end{aligned}$$

where $\hat{S}_{\alpha ij}^{(is)}$ does not depend on time. Here we use the fact that $|k_{\alpha j}^{(is)}\rangle$ is the eigenstate of the Hamiltonian $\hat{H}_\alpha^{(is)}$, and $\exp(i\hat{H}_{S\alpha}^{(is)} t)|k_{\alpha j}^{(is)}\rangle = \exp(i\omega_{\alpha j}^{(is)} t)|k_{\alpha j}^{(is)}\rangle$ and $\langle k_{\alpha j}^{(is)} | \exp(-i\hat{H}_{S\alpha}^{(is)} t) = \langle k_{\alpha j}^{(is)} | \exp(-i\omega_{\alpha j}^{(is)} t)$. It should be noted that the operator $\hat{S}_{\alpha ij}^{(is)}$ corresponds to transition of the subsystem α from the state $|k_{\alpha j}^{(is)}\rangle$ to the state $|k_{\alpha i}^{(is)}\rangle$.

If the unified system $\hat{H}_S^{(is)}$ interacts only with one reservoir $\hat{H}_{R\alpha}$ then the standard procedure leads to the Lindblad superoperator [16]

$$\begin{aligned}
\hat{L}_\alpha[\hat{\rho}_S(t)] &\equiv \sum_{\alpha ij} \lambda_\alpha^2 G_\alpha\left(\Delta\omega_{\alpha ij}^{(is)}\right) \left\{\left[\hat{S}_{\alpha ij}^{(is)}, \hat{\rho}_S(t)\hat{S}_{\alpha ij}^{(is)\dagger}\right]\right. \\
&\left.+ \left[\hat{S}_{\alpha ij}^{(is)}\hat{\rho}_S(t), \hat{S}_{\alpha ij}^{(is)\dagger}\right]\right\}, \quad (A4)
\end{aligned}$$

where $\hat{\rho}_S(t)$ is the density matrix of the big system and $\lambda_\alpha^2 G_\alpha(\Delta\omega_{\alpha ij}^{(is)})$ is the relaxation rate. In the more general case when the system $\hat{H}_S^{(is)}$ interacts with the set of the reservoirs $\hat{H}_R = \sum_\alpha \hat{H}_{R\alpha}$ and these reservoirs are uncorrelated $\langle \hat{R}_\alpha \hat{R}_\beta \rangle = 0$, the standard procedure leads to the Lindblad superoperator of separate subsystems [16,17]

$$\begin{aligned}
\hat{L}[\hat{\rho}_S(t)] &\equiv \sum_\alpha \sum_{ij} \lambda_\alpha^2 G_\alpha\left(\Delta\omega_{\alpha ij}^{(is)}\right) \left\{\left[\hat{S}_{\alpha ij}^{(is)}, \hat{\rho}_S(t)\hat{S}_{\alpha ij}^{(is)\dagger}\right]\right. \\
&\left.+ \left[\hat{S}_{\alpha ij}^{(is)}\hat{\rho}_S(t), \hat{S}_{\alpha ij}^{(is)\dagger}\right]\right\} \\
&= \sum_{\text{subsystem}} \hat{L}_{\text{subsystem}}[\hat{\rho}_S(t)]. \quad (A5)
\end{aligned}$$

Thus, in the case when the subsystems do not interact, the Lindblad superoperator reduces to the sum of the superoperators for isolated subsystems [17,20].

Now we consider the case when the subsystems can interact with each other, i.e., $\varepsilon \neq 0$ in the Hamiltonian (1), and develop the perturbation theory for the Lindblad superoperators. We suppose that despite the fact that the subsystems

interact with each other, the interaction of each subsystem with its own reservoir remains the same, as in the case of noninteracting subsystems [see Eq. (1)].

The procedure described in the preceding section covers the case $\varepsilon = 0$. In the case $\varepsilon \neq 0$, the Lindblad superoperator (A5) is not correct despite the fact that the reservoirs and the interaction between reservoirs and systems remains unchanged. The Lindblad superoperator (A5) has been obtained by employing the basis of the system eigenstates $|k_{\alpha i}^{(is)}\rangle\langle k_{\alpha j}^{(is)}|$. If $\varepsilon \neq 0$, these basis states are not the eigenstates of the Hamiltonian $\hat{H}_S$ and now

$$\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar) \neq \sum_{ij} \hat{S}_{\alpha ij}^{(is)} \exp\left(-i\Delta\omega_{\alpha ij}^{(is)} t\right). \quad (A6)$$

To employ the standard algorithm, we should find new operators $\hat{S}_{\alpha\Delta\omega_{ij}} = \langle k_i | \hat{S}_\alpha | k_j \rangle | k_i \rangle \langle k_j |$, where $|k_j\rangle$ are eigenstates, ω_j are eigenfrequencies of the Hamiltonian $\hat{H}_S$, and $\Delta\omega_{ij} = \omega_i - \omega_j$. However, now the subsystems are not isolated; therefore, the eigenstates $|k_j\rangle$ and eigenfrequencies ω_j of the Hamiltonian $\hat{H}_S$ of interacting subsystems are unknown, so the operators $\hat{S}_{\alpha\Delta\omega_{ij}}$ are also unknown. In the general case, this problem cannot be solved analytically. Moreover, the numerical solution is usually difficult to implement. As an alternative, we develop the perturbation theory for the Lindblad superoperator.

The perturbation theory for the Lindblad superoperator developed here is based on searching for the approximate expansion for the operator $\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar)$ in the form

$$\begin{aligned}
&\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar) \\
&= \sum_{\Delta\omega^{(0)}} \hat{S}_{\Delta\omega^{(0)}}^{(0)} \exp(-i\Delta\omega^{(0)} t) + \varepsilon^1 \\
&\times \sum_{\Delta\omega^{(1)}} \hat{S}_{\Delta\omega^{(1)}}^{(1)} \exp(-i\Delta\omega^{(1)} t) + \cdots, \quad (A7)
\end{aligned}$$

where the operators $\hat{S}_{\Delta\omega^{(n)}}^{(n)}$ do not depend on time. The expansion (A7) is to be found by means of the perturbation theory for a small parameter ε. Once the expansion (A7) is found we can directly apply the standard procedure using the expansion (A7) to obtain the Lindblad superoperators in a power series of ε,

$$\hat{L}[\hat{\rho}_S(t)] = \sum_{n=0}^{+\infty} \varepsilon^n \hat{L}^{(n)}[\hat{\rho}_S(t)]. \quad (A8)$$

Below we show how $\hat{L}^{(n)}[\hat{\rho}_S(t)]$ can be obtained. The starting point for our perturbation theory is the expansion for the operators $\hat{S}_\alpha$ (A1). The expansion (A1) is still valid because the set of the states $|k_{\alpha i}^{(is)}\rangle$ is still the complete basis of the whole system. We substitute the expansion (A1) into the expression $\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar)$ and arrive at the expression

$$\begin{aligned}
&\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar) \\
&= \sum_{ij} \exp(i\hat{H}_S t/\hbar)\hat{S}_{\alpha ij}^{(is)} \exp(-i\hat{H}_S t/\hbar) = \sum_{ij} \hat{\mathbf{S}}_{\alpha ij}(t). \quad (A9)
\end{aligned}$$

For convenience, we introduce new operators

$$\hat{\mathbf{S}}_{\alpha ij}(t) = \exp(i\hat{H}_S t/\hbar)\hat{S}_{\alpha ij}^{(is)} \exp(-i\hat{H}_S t/\hbar). \tag{A10}$$

Now the standard procedure demands the operator $\hat{\mathbf{S}}_{\alpha ij}(t)$ to be presented in the form

$$\hat{\mathbf{S}}_{\alpha ij}(t) = \sum_{\Delta\tilde{\omega}} \hat{\mathbf{S}}'_{\Delta\tilde{\omega}} \exp(-i\Delta\tilde{\omega}t), \tag{A11}$$

where the operators $\hat{\mathbf{S}}'_{\Delta\tilde{\omega}}$ do not depend on time and $\Delta\tilde{\omega}$ are some yet unknown frequencies. The substitution of the expansion (A11) into the expression (A9) allows us to directly apply the standard procedure to obtain the exact Lindblad superoperators. Below we show how the expansion (A11) is obtained by means of the perturbation theory. To find the expansion (A11) we take the time derivative from both sides of (A10). As a result, we obtain the equation for the operators $\hat{\mathbf{S}}_{\alpha ij}(t)$,

$$d\hat{\mathbf{S}}_{\alpha ij}(t)/dt = -i\Delta\omega_{\alpha ij}^{(is)}\hat{\mathbf{S}}_{\alpha ij}(t) + \varepsilon\frac{i}{\hbar}[\hat{W}(t), \hat{\mathbf{S}}_{\alpha ij}(t)], \tag{A12}$$

where the operator $\hat{W}(t)$ is the operator of subsystems interaction, taken in the Heisenberg representation as [55]

$$\hat{W}(t) = \exp(i\hat{H}_S t/\hbar)\hat{W} \exp(-i\hat{H}_S t/\hbar). \tag{A13}$$

The initial condition for Eq. (A12) follows from the definition (A10) at $t = 0$ and has the form

$$\hat{\mathbf{S}}_{\alpha ij}(0) = \hat{S}_{\alpha ij}^{(is)}. \tag{A14}$$

To obtain the expansion (A11), one may solve Eq. (A12) with the initial condition (A14). It is easier to perform this by employing the perturbation theory. We expand the operators $\hat{\mathbf{S}}_{\alpha ij}(t)$ in a series of the small parameter ε,

$$\hat{\mathbf{S}}_{\alpha ij}(t) = \hat{\mathbf{S}}_{\alpha ij}^{(0)}(t) + \varepsilon\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t) + \cdots. \tag{A15}$$

To solve Eq. (A12) with the perturbation theory, we should expand $\hat{W}(t)$ in a series of the small parameter ε as well,

$$\hat{W}(t) = \hat{W}^{(0)}(t) + \varepsilon\hat{W}^{(1)}(t) + \cdots. \tag{A16}$$

We substitute these expansions for $\hat{\mathbf{S}}_{\alpha ij}(t)$ and $\hat{W}(t)$ in Eq. (A12) and equate factors at the same powers of ε. As a result, we obtain up to the second power

$$d\hat{\mathbf{S}}_{\alpha ij}^{(0)}(t)/dt = -i\Delta\omega_{\alpha ij}^{(is)}\hat{\mathbf{S}}_{\alpha ij}^{(0)}(t), \quad \hat{\mathbf{S}}_{\alpha ij}^{(0)}(0) = \hat{S}_{\alpha \Delta\omega_{\alpha ij}^{(is)}}^{(is)}, \tag{A17}$$

$$d\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t)/dt = -i\Delta\omega_{\alpha ij}^{(is)}\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t) + \frac{i}{\hbar}[\hat{W}^{(0)}(t), \hat{\mathbf{S}}_{\alpha ij}^{(0)}(t)],$$
$$\hat{\mathbf{S}}_{\alpha ij}^{(1)}(0) = 0, \tag{A18}$$

$$d\hat{\mathbf{S}}_{\alpha ij}^{(2)}(t)/dt = -i\Delta\omega_{\alpha ij}^{(is)}\hat{\mathbf{S}}_{\alpha ij}^{(2)}(t) + \frac{i}{\hbar}[\hat{W}^{(1)}(t), \hat{\mathbf{S}}_{\alpha ij}^{(0)}(t)]$$
$$+ \frac{i}{\hbar}[\hat{W}^{(0)}(t), \hat{\mathbf{S}}_{\alpha ij}^{(1)}(t)], \quad \hat{\mathbf{S}}_{\alpha ij}^{(2)}(0) = 0. \tag{A19}$$

The solution of Eq. (A17) is

$$\hat{\mathbf{S}}_{\alpha ij}^{(0)}(t) = \hat{S}_{\alpha ij}^{(0)} \exp(-i\Delta\omega_{\alpha ij}^{(is)}t), \tag{A20}$$

where $\hat{S}_{\alpha ij}^{(0)} = \hat{S}_{\alpha ij}^{(is)}$. Note that the expression (A20) has the form (A11). Moreover, the expansion of (A11) in the zeroth order of the perturbation theory takes the form

$$\exp(i\hat{H}_S t/\hbar)\hat{S}_\alpha \exp(-i\hat{H}_S t/\hbar)$$
$$\approx \sum_{\alpha ij} \hat{\mathbf{S}}_{\alpha ij}^{(0)}(t) = \sum_{\alpha ij} \hat{S}_{\alpha ij}^{(0)} \exp(-i\Delta\omega_{\alpha ij}^{(is)}t). \tag{A21}$$

Since $\hat{S}_{\alpha ij}^{(0)} = \hat{S}_{\alpha ij}^{(is)}$, the expansion (A21) is equal to the expansion (A3). If we now apply the standard procedure using the expansion (A21), we will obtain the Lindblad superoperator (22). The Lindblad superoperator (22) is equal to the Lindblad superoperator (A5); thus the Lindblad superoperator in the zeroth order of the perturbation theory developed coincides with the local Lindblad superoperator.

To solve the higher orders of the perturbation theory we use the explicit form (13) for the interaction operator $\hat{W}$. Employing (A13) and (A10) we get

$$\hat{W}(t) = \exp(i\hat{H}_S t/\hbar)\hbar \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2} \hat{S}_{\alpha_1 i_1 j_1}^{(0)} \hat{S}_{\alpha_2 i_2 j_2}^{(0)}$$
$$\exp(-i\hat{H}_S t/\hbar)$$
$$= \hbar \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2} \hat{\mathbf{S}}_{\alpha_1 i_1 j_1}(t) \hat{\mathbf{S}}_{\alpha_2 i_2 j_2}(t). \tag{A22}$$

Substituting the expansions (A15) and (A16) into the expression (A22), we can express the terms $W^{(n)}(t)$ through the terms $\hat{\mathbf{S}}_{\alpha ij}^{(m)}(t)$ as follows:

$$W^{(n)}(t) = \hbar \sum_{n_1 + n_2 = n} \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2} \hat{\mathbf{S}}_{\alpha_1 i_1 j_1}^{(n_1)}(t) \hat{\mathbf{S}}_{\alpha_2 i_2 j_2}^{(n_2)}(t). \tag{A23}$$

Returning to the first order of the perturbation theory, we should substitute $W^{(0)}(t)$ and (A20) into (A18). As a result, we arrive at

$$d\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t)/dt = -i\Delta\omega_{\alpha ij}^{(is)}\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t) + i\sum_{\alpha_1 \neq \alpha_2}\sum_{i_1 j_1 i_2 j_2} w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2}[\hat{S}_{\alpha_1 i_1 j_1}^{(0)}\hat{S}_{\alpha_2 i_2 j_2}^{(0)}, \hat{S}_{\alpha ij}^{(0)}] \exp[-i(\Delta\omega_{\alpha_1 i_1 j_1}^{(is)} + \Delta\omega_{\alpha_2 i_2 j_2}^{(is)} + \Delta\omega_{\alpha ij}^{(is)})t],$$
$$\hat{\mathbf{S}}_{\alpha ij}^{(1)}(0) = 0. \tag{A24}$$

The solution to Eq. (A24) is

$$\hat{\mathbf{S}}_{\alpha ij}^{(1)}(t) = \sum_{\alpha_1 \neq \alpha_2}\sum_{i_1 j_1 i_2 j_2} \frac{w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2}[\hat{S}_{\alpha_1 i_1 j_1}^{(0)}\hat{S}_{\alpha_2 i_2 j_2}^{(0)}, \hat{S}_{\alpha ij}^{(0)}]}{\Delta\omega_{\alpha_1 i_1 j_1}^{(is)} + \Delta\omega_{\alpha_2 i_2 j_2}^{(is)}}\{1 - \exp[-i(\Delta\omega_{\alpha_1 i_1 j_1}^{(is)} + \Delta\omega_{\alpha_2 i_2 j_2}^{(is)})t]\}\exp(-i\Delta\omega_{\alpha ij}^{(is)}t). \tag{A25}$$

Note that if some frequencies $\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}$ are equal to zero, that is, secular terms appear, it is necessary to use the method of multiple scales [56]. In this case one obtains the corrections to the frequencies $\Delta\omega^{(is)}_{\alpha i j}$. Below, for simplicity we assume that all the frequencies $\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}$ in the sum (A25) are not equal to zero when $w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2} \neq 0$. Thus, the solution of Eq. (A12) up to the first order by ε takes the form

$$
\exp(i\hat{H}_S t/\hbar)\hat{S}^{(0)}_{\alpha i j}\exp(-i\hat{H}_S t/\hbar) = \hat{\mathbf{S}}_{\alpha i j}(t) \approx \hat{\mathbf{S}}^{(0)}_{\alpha i j}(t) + \varepsilon\hat{\mathbf{S}}^{(1)}_{\alpha i j}(t)
$$

$$
= \hat{S}^{(0)}_{\alpha i j}\exp\left(-i\Delta\omega^{(is)}_{\alpha i j}t\right) + \varepsilon\sum_{\alpha_1 \neq \alpha_2}\sum_{i_1 j_1 i_2 j_2}\frac{w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2}\big[\hat{S}^{(0)}_{\alpha_1 i_1 j_1}\hat{S}^{(0)}_{\alpha_2 i_2 j_2}, \hat{S}^{(0)}_{\alpha i j}\big]}{\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}}
$$

$$
\times\left\{1 - \exp\left[-i\left(\Delta\omega^{(is)}_{\alpha_1 i_1 j_1} + \Delta\omega^{(is)}_{\alpha_2 i_2 j_2}\right)t\right]\right\}\exp\left(-i\Delta\omega^{(is)}_{\alpha i j}t\right). \tag{A26}
$$

The expansion (28) according to the general theory leads to the Lindblad superoperator (29). The higher orders of the perturbation theory can be obtained in the same way.

Above we assumed that the interaction between the subsystems (13) is defined by the same operators that are present in the system-environment interaction [Eq. (2)]. If this assumption is not fulfilled, the theory developed can be straightforwardly generalized to be applied to such cases in finite-dimensional problems. Here we briefly discuss this generalization. Suppose the interaction (13) contains the operators, which are not present in system-reservoir interaction (2). Then the Heisenberg equation for the first-order approximation (A18) will contain some new operators of zeroth order, which appear due to the commutator $[\hat{W}^{(0)}(t), \hat{S}^{(0)}_{\alpha i j}(t)]$. To make the system of operator equations (A18) closed one needs to write down the Heisenberg equation for new operators appearing in the zeroth order. Thus, for the finite-dimensional case, we obtain a finite-dimensional linear system, which can be solved exactly. The same generalization can be done for higher orders of the perturbation theory.

APPENDIX B: PROOF OF EQS. (34) AND (35)

We start with the proof of Eq. (34). The substitution of Eq. (22) into the left-hand side of Eq. (34) leads to

$$
\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\hat{L}^{(0)}[\hat{\bar{\rho}}_S(t)]\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) = \sum_\alpha\sum_{ij}\lambda_\alpha^2 G_\alpha\left(\Delta\omega^{(is)}_{\alpha i j}\right)\{[\hat{\mathbf{S}}_{\alpha i j}(-t), \hat{\rho}_S(t)\hat{\mathbf{S}}^\dagger_{\alpha i j}(-t)] + [\hat{\mathbf{S}}_{\alpha i j}(-t)\hat{\rho}_S(t), \hat{\mathbf{S}}^\dagger_{\alpha i j}(-t)]\}. \tag{B1}
$$

The difference between the operator $\hat{\mathbf{S}}_{\alpha i j}(t)$ and the operator $\hat{\mathbf{S}}^{(0)}_{\alpha i j}(t)$ is equal to ε. Therefore, we replace the operators $\hat{\mathbf{S}}_{\alpha i j}(t)$ with the operators $\hat{\mathbf{S}}^{(0)}_{\alpha i j}(t)$ in Eq. (B1) and obtain

$$
\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\hat{L}^{(0)}[\hat{\bar{\rho}}_S(t)]\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) \approx \sum_\alpha\sum_{ij}\lambda_\alpha^2 G_\alpha\left(\Delta\omega^{(is)}_{\alpha i j}\right)\{[\hat{\mathbf{S}}^{(0)}_{\alpha i j}(-t), \hat{\rho}_S(t)\hat{\mathbf{S}}^{(0)\dagger}_{\alpha i j}(-t)] + [\hat{\mathbf{S}}^{(0)}_{\alpha i j}(-t)\hat{\rho}_S(t), \hat{\mathbf{S}}^{(0)\dagger}_{\alpha i j}(-t)]\}.
$$
$$\tag{B2}$$

The substitution of Eq. (21) into Eq. (B2) leads to Eq. (34).

Equation (35) can be proved in the same way. To prove Eq. (35) we rewrite the Lindblad superoperator $\hat{L}^{(0)}[\hat{\bar{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\bar{\rho}}_S(t)]$ in the form

$$
\hat{L}^{(0)}[\hat{\bar{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\bar{\rho}}_S(t)] \approx \sum_\alpha\sum_{ij}\lambda_\alpha^2 G_\alpha\left(\Delta\omega^{(is)}_{\alpha i j}\right)\{\big[\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big), \hat{\bar{\rho}}_S(t)\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)^\dagger\big]
$$

$$
+ \big[\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)\hat{\bar{\rho}}_S(t), \big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)^\dagger\big]\}. \tag{B3}
$$

The substitution of Eq. (B3) into Eq. (35) leads to

$$
\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\{\hat{L}^{(0)}[\hat{\bar{\rho}}_S(t)] + \varepsilon\hat{L}^{(1)}[\hat{\bar{\rho}}_S(t)]\}\exp\left(i\frac{\hat{H}_S}{\hbar}t\right)
$$

$$
= \sum_\alpha\sum_{ij}\lambda_\alpha^2 G_\alpha\left(\Delta\omega^{(is)}_{\alpha i j}\right)\left\{\left[\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)\exp\left(i\frac{\hat{H}_S}{\hbar}t\right), \hat{\rho}_S(t)\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)^\dagger\exp\left(i\frac{\hat{H}_S}{\hbar}t\right)\right]\right.
$$

$$
\left. + \left[\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)\exp\left(i\frac{\hat{H}_S}{\hbar}t\right)\hat{\rho}_S(t), \exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\big(\hat{S}^{(0)}_{\alpha i j} + \varepsilon\hat{S}^{(1)}_{\alpha i j}\big)^\dagger\exp\left(i\frac{\hat{H}_S}{\hbar}t\right)\right]\right\}. \tag{B4}
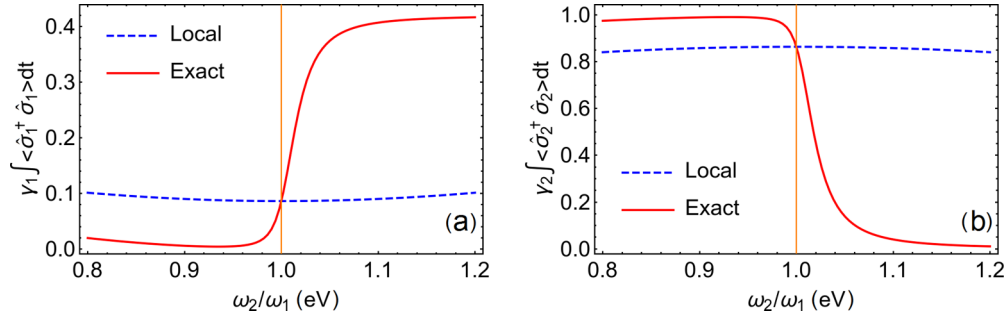$$

FIG. 5. Occupancies integrated over time for the excitation transfer problem, (a) $\gamma_1 \int_0^{+\infty} \langle \hat{\sigma}_1^\dagger \hat{\sigma}_1 \rangle dt$ and (b) $\gamma_2 \int_0^{+\infty} \langle \hat{\sigma}_2^\dagger \hat{\sigma}_2 \rangle dt$, plotted as functions of the ratio of the TLSs' excitation frequencies ω_2/ω_1. The parameters of the system are the same as in Fig. 1: $g = 0.01\omega_1$, $\Gamma_1 = \Gamma_2 = 10^{-3}\omega_1$, $\gamma_1 = 10^{-6}\omega_1$, $\gamma_2 = 10^{-7}\omega_1$, and temperature $T = 0$. Blue dashed lines represent the solutions of the local Lindblad equation, red solid lines represent the solution of the exact Lindblad equation, and vertical orange lines indicate the degenerate case $\omega_2/\omega_1 = 1$.

Let us consider the operator $\exp(-i\hat{H}_S t/\hbar)(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)}) \exp(i\hat{H}_S t/\hbar)$. We use the definitions (28) and (A10) and obtain

$$\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\left(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)}\right)\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) = \hat{\mathbf{S}}_{\alpha ij}(-t) + \sum_{\alpha_1 \neq \alpha_2} \sum_{i_1 j_1 i_2 j_2} \frac{w_{\alpha_1 \alpha_2 i_1 j_1 i_2 j_2}\left[\hat{\mathbf{S}}_{\alpha_1 i_1 j_1}(-t)\hat{\mathbf{S}}_{\alpha_2 i_2 j_2}(-t), \hat{\mathbf{S}}_{\alpha ij}(-t)\right]}{\Delta\omega_{\alpha_1 i_1 j_1}^{(is)} + \Delta\omega_{\alpha_2 i_2 j_2}^{(is)}}. \quad (B5)$$

The substitution of Eq. (27) into Eq. (B5) leads to the approximate equality

$$\exp\left(-i\frac{\hat{H}_S}{\hbar}t\right)\left(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)}\right)\exp\left(i\frac{\hat{H}_S}{\hbar}t\right) \approx \left(\hat{S}_{\alpha ij}^{(0)} + \varepsilon \hat{S}_{\alpha ij}^{(1)}\right)\exp\left(-i\Delta\omega_{\alpha ij}^{(is)}t\right). \quad (B6)$$

The difference between the left-hand side and the right-hand side of Eq. (B6) is proportional to ε^2. The substitution of Eq. (B6) into Eq. (B4) leads to the approximate equality (35).

APPENDIX C: APPLICABILITY OF LOCAL LINDBLAD EQUATIONS FOR DEGENERATE SYSTEMS

In this appendix we consider the applicability of the local Lindblad equations for the degenerate systems, i.e., when the subsystems have the same excitation energies.

The local Lindblad equation leads to erroneous energy transitions between the subsystems. These erroneous energy transitions require additional energy, which is of the order of the energy mismatch between the subsystems. The reservoirs provide the additional energy to the system. If the dissipations in the system do not compensate for this energy flow from the reservoirs, violation of the second law of thermodynamics occurs. Keeping in mind this mechanism, one should expect that the local Lindblad equations for the degenerate subsystems should be thermodynamically consistent. Indeed, the erroneous excitation transitions between the subsystems,

caused by application the local Lindblad equations, would not require the additional energy in the degenerate case.

We illustrate the above arguments in Fig. 5, which shows a comparison between the results obtained with the local Lindblad equation and exact Lindblad equation. As an example we consider the excitation transfer problem between two TLSs with transitions frequencies ω_1 and ω_2. The first TLS is initially in the excited state and the second one is in the ground state. To characterize the excitation transfer from the first TLS to the second TLS we use their occupancies integrated over time, $\gamma_1 \int_0^{+\infty} \langle \hat{\sigma}_1^\dagger \hat{\sigma}_1 \rangle dt$ and $\gamma_2 \int_0^{+\infty} \langle \hat{\sigma}_2^\dagger \hat{\sigma}_2 \rangle dt$. One can see that for the degenerate case ($\omega_2/\omega_1 \approx 1$) the local Lindblad equations and exact Lindblad equations give the same results, i.e., the zeroth order of perturbation theory is quantitatively correct. Thus, for the problem of quantum transport, it is the nondegenerate case that requires special attention.

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