Slippage of initial conditions for the Redfield master equation

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For a slow open quantum subsystem weakly coupled to a fast thermal bath, we derive the general form of the slippage to be applied to the initial conditions of the Redfield master equation. This slippage is given by a superoperator which describes the non-Markovian dynamics of the subsystem during the short-time relaxation of the thermal bath. We verify on an example that the Redfield equation preserves positivity after that the slippage superoperator has been applied to the initial density matrix of the subsystem. For δ-correlated baths, the Redfield master equation reduces to the Lindblad master equation and the slippage of initial conditions vanishes consistently.

I. INTRODUCTION

A major preoccupation of our field is to describe the time evolution of a small system coupled to a larger system which serves as a reservoir or thermal bath. This problem is essential to understand reactions in condensed phases such as liquids and solids.

On one hand, for a classical dynamics, several master equations of the Chapman-Kolmogorov type have been derived in order to describe the time evolution of the probability density of the subsystem variables, such as the Fokker-Planck equation for the Brownian motion [1], the Boltzmann-Lorentz linear equation for the diffusion of tracers in fluids [2], or the birth-and-death master equation for nonequilibrium reacting systems [3, 4].

On the other hand, Pauli derived in 1928 a master equation for the occupation probabilities of a quantum subsystem interacting with the environment [5]. Since then, methods have been developed in order to derive the quantum master equation which rules the time evolution of the density matrix describing a quantum subsystem. In the seventies, Lindblad derived the most general quantum master equation which is Markovian and which preserves positivity during the whole time evolution [6]. This master equation has been applied to many systems, especially, those in quantum optics [7]. However, the applicability of the Lindblad master equation is restricted to such baths that the time correlation functions of the coupling operators to the bath or environment, are proportional to the Dirac delta distribution, the so-called δ-correlated baths. This assumption is well justified in quantum optics because the light-matter interaction is the fastest possible one according to relativity, leading to a Markovian process.

In the late fifties, using the second-order perturbation theory, Redfield derived a master equation which is valid for more general baths than the δ-correlated ones [8]. The Redfield master equation has been applied to many systems where the bath has a faster dynamics than the subsystem, as it is the case in NMR where the subsystem is one spin coupled to the other spins and to the phonons. Since then, the Redfield master equation has been used as a reference master equation because it can be systematically derived from the principles of quantum mechanics, in spite of its restriction to the case of weak coupling.

However, it is also known that the Redfield master equation breaks the positivity of the density matrix for initial conditions near the border of the space of physically admissible density matrices. This problem has been much discussed in the recent literature [9–11]. It has been argued that the violation of positivity should arise if memory effects are not adequately taken into account at the initial stage of the time evolution [10]. In this regard, Suarez, Silbey and Oppenheim have suggested to apply a slippage of the initial conditions before starting the time evolution under the Redfield equation [10]. However, these authors have formulated their suggestion for the spin-boson model [12] and they did not proposed a general expression for this slippage.

The aim of the present paper is to derive systematically the general slippage of initial conditions by using the second-order perturbation theory. This slippage should take into account the effects of the non-Markovian evolution of the subsystem during the short-time relaxation of the thermal bath. After this slippage of initial conditions the time evolution under the Redfield master equation should preserve the positivity of the reduced density matrix of the subsystem.

The plan of the paper is as follows. In Sec. II, we summarize the derivation of the Redfield master equation and we fix our notations. In Sec. III, we obtain the general slippage of initial conditions to be used with the Redfield master equation. In Sec. IV, we show that the Lindblad master equation can be recovered for the limit of δ-correlated baths and that the slippage vanishes consistently in the same limit. In Sec. V, the results are applied to the spin-boson model for which we verify that positivity is preserved by the Redfield equation after that the initial conditions are slipped by the slippage superoperator obtained in Sec. III. Conclusions are finally drawn in Sec. VI.

II.   THE REDFIELD MASTER EQUATION

We suppose that a subsystem of Hamiltonian H_s is coupled to a bath of Hamiltonian H_b by an interaction potential λV, where λ is the coupling parameter. The total Hamiltonian of this coupled system is thus

$$H = H_0 + \lambda V = H_s + H_b + \lambda V . \tag{1}$$

The potential is assumed to have the form

$$V = V^\dagger = \sum_\alpha S_\alpha B_\alpha , \tag{2}$$

where S_α and B_α are subsystem and bath operators, respectively. The potential is in general a Hermitian operator but S_α and B_α may be non-Hermitian. Nevertheless, they can always be redefined as Hermitian operators as shown in Appendix A.

The total system is described by a density matrix $\rho(t)$ evolving in time under the Landau-von Neumann differential equation

$$\dot{\rho}(t) = - i [H, \rho(t)] \equiv \mathcal{L} \rho(t) , \tag{3}$$

which defines the quantum Liouvillian superoperator $\mathcal{L}$.

In order to obtain the time evolution of the density matrix by perturbation theory, it is convenient to introduce the interaction representation where

$$\rho_I(t) \equiv \exp(iH_0 t) \rho(t) \exp(-iH_0 t) , \tag{4}$$
$$V_I(t) \equiv \exp(iH_0 t) V \exp(-iH_0 t) , \tag{5}$$

so that the evolution equation becomes

$$\dot{\rho}_I(t) = - i [\lambda V_I(t), \rho_I(t)] \equiv \mathcal{L}_I(t) \rho_I(t) , \tag{6}$$

which defines the Liouvillian in the interaction representation $\mathcal{L}_I(t)$. Eq. (6) can be integrated over time and expanded in a power series of the coupling parameter λ to obtain a perturbative expansion for the density matrix at the current time t

$$\rho_I(t) = \rho(0) + \int_0^t dt_1 \, \mathcal{L}_I(t_1) \, \rho(0)$$
$$+ \int_0^t dt_1 \int_0^{t_1} dt_2 \, \mathcal{L}_I(t_1) \, \mathcal{L}_I(t_2) \, \rho(0) + \mathcal{O}(\lambda^3) . \tag{7}$$

For simplicity, the initial conditions are supposed to be products of an arbitrary density matrix for the subsystem with a density matrix of the canonical ensemble for the bath

$$\rho(0) = \rho_s(0) \rho_b^{eq} , \quad \text{with} \quad \rho_b^{eq} = \frac{\exp(-\beta H_b)}{\text{tr}_b \exp(-\beta H_b)} , \tag{8}$$

where tr_b denotes a partial trace over the bath quantum states.

The purpose of the theory is to study the *reduced density matrix* of the subsystem which is defined by tracing out the bath degrees of freedom as

$$\rho_{\mathrm{sI}}(t) \; \equiv \; \mathrm{tr}_{\mathrm{b}} \; \rho_{\mathrm{I}}(t) \; , \tag{9}$$

in the interaction representation. Accordingly, the reduced density matrix of the original representation becomes

$$\rho_{\mathrm{s}}(t) \; \equiv \; \mathrm{tr}_{\mathrm{b}} \; \rho(t) \; = \; \exp(-iH_{\mathrm{s}}t) \; \rho_{\mathrm{sI}}(t) \; \exp(iH_{\mathrm{s}}t) \; \equiv \; e^{\mathcal{L}_{\mathrm{s}}t} \; \rho_{\mathrm{sI}}(t) \; . \tag{10}$$

We assume that $\mathrm{tr}_{\mathrm{b}}(\rho_{\mathrm{b}}^{\mathrm{eq}}V) = 0$, otherwise we would have to redefine the potential and subsystem Hamiltonian as follows

$$\begin{aligned}
V &\; \longrightarrow \; V \; - \; \mathrm{tr}_{\mathrm{b}} \; \rho_{\mathrm{b}}^{\mathrm{eq}} \; V \; , \\
H_{\mathrm{s}} &\; \longrightarrow \; H_{\mathrm{s}} \; + \; \lambda \; \mathrm{tr}_{\mathrm{b}} \; \rho_{\mathrm{b}}^{\mathrm{eq}} \; V \; , \\
H_{\mathrm{b}} &\; \longrightarrow \; H_{\mathrm{b}} \; .
\end{aligned} \tag{11}$$

The purpose of this redefinition is to include the first-order perturbation inside the zeroth-order Hamiltonian of the subsystem and, hence, to deal directly with the second-order perturbation.

The time evolution of the reduced density matrix can now be obtained by replacing the perturbative series (7) inside the definition (10) and by using the assumption (8) for the initial condition. Since the first-order term disappears because of (11), after a change of time variables to $\tau = t_1 - t_2$ and $T = t_1$, we obtain the second-order expression [4]

$$\rho_{\mathrm{s}}(t) \; = \; e^{\mathcal{L}_{\mathrm{s}}t}\rho_{\mathrm{s}}(0) \; + \; \int_0^t dT \int_0^T d\tau \; e^{\mathcal{L}_{\mathrm{s}}(t-T)} \; \mathcal{C}(\tau) \; e^{\mathcal{L}_{\mathrm{s}}T}\rho_{\mathrm{s}}(0) \; + \; \mathcal{O}(\lambda^3) \; , \tag{12}$$

which plays a central role in the following. In Eq. (12), we have defined the correlation superoperator

$$\mathcal{C}(\tau) \; \equiv \; \mathrm{tr}_{\mathrm{b}} \left[\mathcal{L}_{\mathrm{I}}(0)\mathcal{L}_{\mathrm{I}}(-\tau)\rho_{\mathrm{b}}^{\mathrm{eq}} \right] \; = \; \mathrm{tr}_{\mathrm{b}} \left[\mathcal{L}_{\mathrm{I}} \; e^{\mathcal{L}_0\tau} \; \mathcal{L}_{\mathrm{I}} \; e^{-\mathcal{L}_0\tau} \rho_{\mathrm{b}}^{\mathrm{eq}} \right] \; , \tag{13}$$

where $\mathcal{L}_0 = \mathcal{L}_{\mathrm{s}} + \mathcal{L}_{\mathrm{b}}$ is the zeroth-order Liouvillian. This superoperator still acts on the subsystem degrees of freedom because the trace has been carried out only on the bath degrees of freedom. We remark that the superoperator (13) involves the time correlation functions of the bath operators B_α.

If Eq. (12) is differentiated with respect to the time t, we obtain the following differential equation for the reduced density matrix of the subsystem

$$\frac{d\rho_{\mathrm{s}}(t)}{dt} \; = \; \left[\mathcal{L}_{\mathrm{s}} \; + \; \int_0^t d\tau \; \mathcal{C}(\tau) \; + \; \mathcal{O}(\lambda^3) \right] \rho_{\mathrm{s}}(t) \; . \tag{14}$$

We notice that the right-hand member of this equation depends explicitly on the time because the superoperator (13) is integrated over the finite time interval between the initial time $t = 0$ and the current time t. Accordingly, the master equation (14) is non-Markovian.

If the thermal bath is sufficiently large we may assume that its dynamics has the mixing property and that its time correlation functions decay fast enough to zero for times τ longer than the relaxation time t_{b} of the bath: $\tau \gg t_{\mathrm{b}}$. Therefore, if we are interested in the dynamics of the subsystem over times which are longer than the bath relaxation time, $t \gg t_{\mathrm{b}}$, the integral over the time in Eq. (14) converges to a constant superoperator. Under this assumption called a Markovian assumption, we obtain the *Redfield master equation* [4, 8]

$$\frac{d\rho_{\mathrm{s}}^{\mathrm{R}}(t)}{dt} \; = \; \left[\mathcal{L}_{\mathrm{s}} \; + \; \int_0^\infty d\tau \; \mathcal{C}(\tau) \; + \; \mathcal{O}(\lambda^3) \right] \rho_{\mathrm{s}}^{\mathrm{R}}(t) \; \equiv \; \mathcal{L}_{\mathrm{s}}^{\mathrm{R}} \; \rho_{\mathrm{s}}^{\mathrm{R}}(t) \; , \tag{15}$$

where $\rho_{\mathrm{s}}^{\mathrm{R}}(t)$ has a time dependence which may differ from that of (12), as explained below. The right-hand member of Eq. (15) defines the Redfield Liouvillian superoperator.

If we introduce the bath correlation functions

$$C_{\alpha\beta}(\tau) \; \equiv \; \mathrm{tr}_{\mathrm{b}} \; \rho_{\mathrm{b}}^{\mathrm{eq}} \; \exp(iH_{\mathrm{b}}\tau) \; B_\alpha \; \exp(-iH_{\mathrm{b}}\tau) \; B_\beta \; , \tag{16}$$

and the operators

$$T_\alpha \; \equiv \; \sum_\beta \int_0^\infty d\tau \; C_{\alpha\beta}(\tau) \; \exp(-iH_{\mathrm{s}}\tau) \; S_\beta \; \exp(iH_{\mathrm{s}}\tau) \; , \tag{17}$$

the Redfield master equation takes the explicit form [13]

$$\frac{d\rho_s^R}{dt} = - i [H_s, \rho_s^R] + \lambda^2 \sum_\alpha \left(T_\alpha \rho_s^R S_\alpha + S_\alpha^\dagger \rho_s^R T_\alpha^\dagger - S_\alpha T_\alpha \rho_s^R - \rho_s^R T_\alpha^\dagger S_\alpha^\dagger \right) + \mathcal{O}(\lambda^3) . \tag{18}$$

During the time evolution, this equation preserves the Hermiticity of the reduced density matrix, $\rho_s^R(t) = \rho_s^{R\dagger}(t)$, as well as its normalization, $\mathrm{tr}_s \rho_s^R(t) = 1$, as shown by a direct verification. However, the Redfield master equation only describes approximately the forward semigroup of the time evolution of the subsystem.

III. POSITIVITY AND THE SLIPPAGE OF INITIAL CONDITIONS

If the space of the quantum states of the subsystem has the dimension N, the reduced density matrix ρ_s has $N \times N$ elements. Because of its Hermitian character, the reduced density matrix can be diagonalized and its eigenvalues are real numbers

$$\rho_s = \sum_{k=1}^N |\psi_k\rangle \, p_k \, \langle\psi_k| , \qquad \text{with} \quad 0 \leq p_k \leq 1 , \tag{19}$$

where the coefficients $\{p_k\}$ are interpreted as the probabilities to find the subsystem in each of the eigenstates $|\psi_k\rangle$. These probabilities should therefore have values contained between zero and one so that we have the property

$$\det \rho_s = \prod_{k=1}^N p_k \geq 0 . \tag{20}$$

The condition (20) together with the normalization $\mathrm{tr}_b \rho_s = 1$ delimit the set (19) of admissible density matrices.

Since the reduced density matrix is Hermitian and normalized to unit probability it can be represented by $N^2 - 1$ real variables, which are the $N(N-1)/2$ real parts of the off-diagonal elements of the density matrix, their $N(N-1)/2$ imaginary parts, plus the $N - 1$ real diagonal elements of the density matrix with the constraint that their sum is unity. These real variables define a $(N^2 - 1)$-dimensional space where the physically admissible density matrices satisfying (19) and (20) form a bounded set with a border beyond which positivity is violated.

Several works have shown that the Redfield master equation does not preserve positivity near the border of the set of physically admissible density matrices [4, 9–11]. Positivity may be violated if the initial condition is close to the aforementioned border. However, the amount by which positivity is violated remains of the second order in the coupling parameter, λ^2.

The work by Suarez, Silbey and Oppenheim has shown that this problem appears when memory effects in the early time evolution are not taken into account [10]. Using the expression (12) given by the second-order perturbation theory, these authors have observed that the reduced density matrix evolves rapidly between the initial time $t = 0$ and a time equal to the bath relaxation time $t \simeq t_b$ (see Fig. 1). Only, for longer times $t > t_b$, the reduced density matrix starts its slow dynamics approximately described by the Redfield master equation. The fast early dynamics turns out to be well described by Eq. (12) which, therefore, produces a slippage of the initial conditions (see Fig. 1). Moreover, Suarez et al. observed that the slippage brings initial conditions from the border of the set of admissible density matrices sufficiently inside this set in order for positivity to be guaranteed by the following evolution under the Redfield master equation (see Fig. 1) [10]. In this regard, a slippage of the initial conditions should provide a satisfactory resolution of the problem of positivity.

We may infer from the work by Suarez et al. [10] that the initial condition to be used in the Redfield master equation (15) should differ from the true initial condition by a slippage superoperator $\mathcal{S}$

$$\rho_s^R(0) = \mathcal{S} \, \rho_s(0) . \tag{21}$$

Consequently, the time evolution should be given by

$$\rho_s(t) \simeq e^{\mathcal{L}_s^R t} \mathcal{S} \, \rho_s(0) , \qquad \text{for} \quad t > t_b . \tag{22}$$

Accordingly, the slippage superoperator $\mathcal{S}$ can be calculated by comparing the early time dynamics of the complete time evolution Eq. (12) with that of the Redfield time evolution (15). Integrating the Redfield master equation (15) up to second order, we get

$$\rho_s^R(t) = e^{\mathcal{L}_s t} \rho_s^R(0) + \int_0^t dT \int_0^\infty d\tau \, e^{\mathcal{L}_s(t-T)} \, \mathcal{C}(\tau) \, e^{\mathcal{L}_s T} \rho_s^R(0) + \mathcal{O}(\lambda^3) , \tag{23}$$
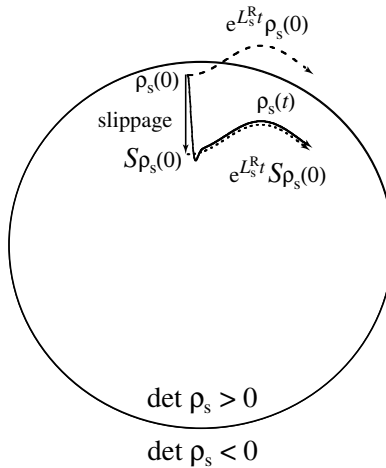
FIG. 1: The space of the reduced matrices ρ_s is divided into the set of admissible density matrices for which $\det \rho_s \geq 0$ (so that all the eigenvalues of ρ_s define non-negative probabilities) and the set of non-admissible density matrices for which $\det \rho_s < 0$. The figure depicts schematically the trajectories of the reduced density matrix for different time evolutions: the Redfield dynamics $\exp(\mathcal{L}_s^R t)\rho_s(0)$ from the non-slipped initial condition $\rho_s(0)$ near the border of the set of admissible density matrices (long-dashed line), which violates positivity; the Redfield dynamics $\exp(\mathcal{L}_s^R t)\mathcal{S}\rho_s(0)$ from the slipped initial condition $\rho_s^R(0) = \mathcal{S}\rho_s(0)$ (short-dashed line); the complete dynamics $\rho_s(t)$ calculated by the formula (12) of the second-order perturbation theory or by the non-Markovian master equation (14) (solid line).

which differs from (12) for times smaller than the bath relaxation time $t < t_b$ as depicted in Fig. 2. We assume that $\rho_s^R(t)$ is approximately equal to $\rho_s(t)$ for intermediate times $t_b \ll t \ll t_s$, where t_s is a characteristic time of the slow dynamics of the subsystem. Therefore, we can approximately equate Eq. (23) to Eq. (12) in order to obtain at second order

$$\rho_s^R(0) \;=\; \rho_s(0) \;-\; \int_0^\infty dT \int_T^\infty d\tau \; e^{-\mathcal{L}_s T} \; \mathcal{C}(\tau) \; e^{\mathcal{L}_s T} \rho_s(0) \;+\; \mathcal{O}(\lambda^3) \;, \tag{24}$$

where we set $t \to \infty$ because of our assumptions that $t_b \ll t \ll t_s$ and that the bath time correlation functions decay to zero sufficiently fast before this intermediate time scale. Exchanging the time integrals over τ and T in (24), we finally obtain the slippage superoperator as

$$\begin{aligned}
\rho_s^R(0) &\;=\; \rho_s(0) \;-\; \int_0^\infty d\tau \int_0^\tau dT \; e^{-\mathcal{L}_s T} \; \mathcal{C}(\tau) \; e^{\mathcal{L}_s T} \rho_s(0) \;+\; \mathcal{O}(\lambda^3) \\
&\;\equiv\; \mathcal{S} \, \rho_s(0) \;,
\end{aligned} \tag{25}$$

in terms of the same correlation superoperator (13) as in the Redfield master equation itself (see Fig. 2). Accordingly, the slippage is of second order in the coupling parameter, λ^2.

If we expand the Liouvillian evolution superoperator $\exp(\mathcal{L}_s T)$ in powers of the time T and if we integrate over the variable T, we obtain

$$\begin{aligned}
\rho_s^R(0) &\;=\; \mathcal{S} \, \rho_s(0) \\
&\;=\; \rho_s(0) \;-\; \int_0^\infty d\tau \left\{ \tau \, \mathcal{C}(\tau) + \frac{\tau^2}{2!} \, [\mathcal{C}(\tau), \mathcal{L}_s] + \frac{\tau^3}{3!} \, [[\mathcal{C}(\tau), \mathcal{L}_s], \mathcal{L}_s] + \cdots \right\} \rho_s(0) + \mathcal{O}(\lambda^3) \;.
\end{aligned} \tag{26}$$

This expansion shows that the slippage is proportional to the relaxation time of the bath t_b. Indeed, if the correlation functions decay over the time t_b then the first term of the slippage, $\int_0^\infty d\tau \, \tau \, \mathcal{C}(\tau)$, is of the same order as the bath relaxation time t_b so that the slippage vanishes as $t_b \to 0$.

We can check that Eq. (25) implies that the Hermitian conjugate relation also holds

$$\rho_s^{R\dagger}(0) \;=\; \mathcal{S} \, \rho_s^\dagger(0) \;. \tag{27}$$

Consequently, the Hermiticity of the reduced density matrix is preserved by the slippage. We also have the property that the normalization is preserved by the slippage

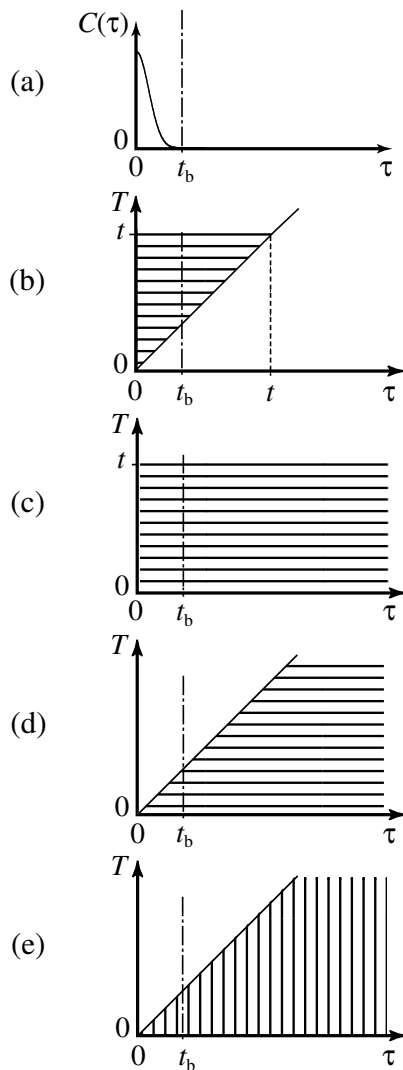$$\mathrm{tr}_s \, \rho_s^R(0) \;=\; \mathrm{tr}_s \, \mathcal{S} \, \rho_s(0) \;=\; 1 \;, \tag{28}$$

FIG. 2: (a) Schematic behavior of a time correlation function of the bath coupling operators. Domains of integration in the plane of the time variables (τ, T) used in: (b) Eq. (12) of second-order pertubation theory; (c) Eq. (23) for the Redfield master equation; (d) Eq. (24) of the slippage; (e) Eq. (25) of the slippage. Since the time correlation functions of the bath vanish essentially for $\tau > t_{\rm b}$, the right-hand side of the vertical dashed-dotted line gives a negligible contribution to the integrals. In every case, the integrated quantity has a slow variation along the T-axis. Therefore, we observe that the integral (b) of second-order perturbation theory has a fast variation for $0 < t < t_{\rm b}$ although the integral (c) of the Redfield theory does not have such a fast variation.

because this normalization is preserved by each Liouvillian superoperator used above.

If we introduce the operators

$$T_\alpha^{(k)} \equiv \sum_\beta \int_0^\infty d\tau \, \frac{\tau^k}{k!} \, C_{\alpha\beta}(\tau) \, \exp(-iH_{\rm s}\tau) \, S_\beta \, \exp(iH_{\rm s}\tau) \, , \tag{29}$$

the slippage superoperator takes the explicit form

$$
\begin{aligned}
\rho_{\rm s}^{\rm R}(0) & = \; \mathcal{S} \, \rho_{\rm s}(0) \\
& = \; \rho_{\rm s}(0) \, + \, \lambda^2 \sum_\alpha \left\{ [S_\alpha, T_\alpha^{(1)} \rho_{\rm s}(0)] \right.
\end{aligned}
$$

$$+ [S_\alpha, T_\alpha^{(2)}[\rho_s(0), iH_s]] - [[S_\alpha, T_\alpha^{(2)}\rho_s(0)], iH_s] + \text{H. c.} + \cdots \Big\} + \mathcal{O}(\lambda^3) \,. \tag{30}$$

For all the initial reduced density matrices with a positive determinant, the slipped reduced density matrix is conjectured to lead to a time evolution under the Redfield master equation which preserves the positivity, at least up to second order in the coupling parameter. This conjecture is motivated by the analysis by Suarez et al. [10].

We notice that the slippage of the initial conditions of the Redfield master equation partially restores the non-Markovian character of the process described by Eq. (14) because the slippage takes into account a memory effect on the time scale of the bath correlation functions. The necessity of a slippage of initial conditions can be understood by the fact that the process described by Eq. (14) is still non-Markovian even if the long-time evolution can be approximated by the Markovian-like Redfield master equation. The non-Markovian character of the process leaves its signature in the fast early dynamics where the slippage occurs.

We should mention that a construction very similar to Eq. (22) has already been derived around 1967 in the broader context of nonequilibrium statistical mechanics [14]. The purpose was to derive the connection between the general non-Markovian master equation and its asymptotic Markovian approximation. In these works, Eq. (21) is called the post-initial condition [14].

IV. δ-CORRELATED BATHS

In this section, we consider the special case where the time correlation functions (16) of the bath coupling operators are proportional to the Dirac δ-distribution

$$C_{\alpha\beta}(\tau) = 2 D_{\alpha\beta} \delta(\tau) \,, \tag{31}$$

where $D_{\alpha\beta}$ is a matrix of constants characterizing the dissipative coupling to the bath. As shown in Appendix A, the coupling operators S_α and B_α can be chosen to be Hermitian, in which case Eq. (16) allows us to show that the matrix $\mathbf{D}$ formed by the elements $D_{\alpha\beta}$ is Hermitian

$$D_{\alpha\beta}^* = D_{\beta\alpha} \,. \tag{32}$$

This matrix can be interpreted as a matrix of generalized diffusion coefficients. As a consequence of (32), the matrix can be diagonalized by a unitary transformation $\mathbf{U}$ as

$$\mathbf{D} = \mathbf{U}^\dagger \cdot \mathbf{d} \cdot \mathbf{U} \,, \tag{33}$$

where $\mathbf{d}$ is a diagonal matrix containing the eigenvalues d_α of (32). If we introduce the Lindblad operators as

$$L_\alpha \equiv \sqrt{d_\alpha} \sum_\beta U_{\alpha\beta} S_\beta \,, \tag{34}$$

the Redfield master equation (18) reduces for δ-correlated baths to the Lindblad master equation [6]

$$\frac{d\rho_s}{dt} = -i [H_s, \rho_s] + \lambda^2 \sum_\alpha \left(2L_\alpha \rho_s L_\alpha^\dagger - L_\alpha^\dagger L_\alpha \rho_s - \rho_s L_\alpha^\dagger L_\alpha \right) + \mathcal{O}(\lambda^3) \,. \tag{35}$$

This equation is known to preserve not only Hermiticity and normalization but also positivity. It is the only equation of a Markovian semigroup which preserves these three properties [6, 9].

In agreement with this result, no slippage is required for δ-correlated baths because the slippage superoperator (25) becomes the identity, $\mathcal{S} = \mathcal{I}$. Indeed, under the assumption (31), the correlation superoperator (13) is proportional to a δ-distribution, $\mathcal{C}(\tau) \sim \delta(\tau)$, and the slippage (25)-(26) vanishes because $\int_0^\infty d\tau \, \tau^k \, \delta(\tau) = 0$ for $k \geq 1$, as expected in the limit $t_b \to 0$.

V. APPLICATION TO THE SPIN-BOSON MODEL

In this section, we apply the theory developed in the previous sections to the spin-boson model in order to verify whether the slippage superoperator (25) reproduces the memory effect originating from the short-time dynamics of the thermal bath and whether the positivity is still violated by the Redfield equation even after our slippage of initial conditions.

The spin-boson model is defined by the total Hamiltonian [10, 12]

$$H = -\frac{\Delta}{2}\,\sigma_z + H_{\rm b} + \lambda\,\sigma_x\,B\;, \tag{36}$$

in terms of the Pauli matrices σ_x, σ_y, and σ_z. The parameter Δ is the energy splitting between the two levels of the subsystem in absence of coupling to the reservoir. The reservoir or thermal bath is a collection of harmonic oscillators of Hamiltonian

$$H_{\rm b} = \frac{1}{2}\,\sum_\alpha\left(p_\alpha^2 + \omega_\alpha^2\,x_\alpha^2\right)\;, \tag{37}$$

while the coupling between the two-level subsystem and the bath is described by the operator

$$B = \sum_\alpha c_\alpha\,x_\alpha\;. \tag{38}$$

The bath is characterized by its spectral strength

$$J(\omega) = \sum_\alpha \frac{c_\alpha^2}{2\omega_\alpha}\,\delta(\omega - \omega_\alpha) = \frac{\omega^3}{\omega_{\rm c}^2}\,\exp(-\omega/\omega_{\rm c})\;, \tag{39}$$

where $\omega_{\rm c}$ is a cutoff frequency [10, 12]. The dimensionless friction constant defined by Suarez et al. in Ref. [10] can here be taken as $\eta = \lambda^2$.

The two-level subsystem can be considered as a spin $s = \frac{1}{2}$. Therefore, the reduced density matrix of the subsystem can be decomposed in the basis formed by Pauli matrices

$$\rho_{\rm s} = \frac{1}{2}\left(1 + x\,\sigma_x + y\,\sigma_y + z\,\sigma_z\right)\;, \tag{40}$$

with three real coefficients x, y, and z. We notice that the normalization $\mathrm{tr}_{\rm s}\rho_{\rm s} = 1$ is satisfied. In this Bloch representation, the determinant of the reduced density matrix is

$$\det\,\rho_{\rm s} = \frac{1}{4}\left(1 - x^2 - y^2 - z^2\right) \geq 0\;, \tag{41}$$

so that the set of admissible density matrices is the so-called Bloch unit sphere, which is the tridimensional sphere of unit radius in the space (x, y, z).

In the Bloch representation, the non-Markovian master equation (14) obtained at the second order of perturbation theory is given for the spin-boson model by the following set of time-dependent, linear, ordinary differential equations

$$\begin{cases} \dot{x} = \Delta\,y\;, \\ \dot{y} = -\left[\Delta + h(t)\right]\,x - g(t)\,y\;, \\ \dot{z} = -\,f(t) - g(t)\,z\;, \end{cases} \tag{42}$$

where the dot denotes a differentiation with respect to time and

$$\begin{cases} f(t) = 4\,\lambda^2\,\int_0^t d\tau\;\sin\Delta\tau\;\mathrm{Im}\,C(\tau)\;, \\ g(t) = 4\,\lambda^2\,\int_0^t d\tau\;\cos\Delta\tau\;\mathrm{Re}\,C(\tau)\;, \\ h(t) = 4\,\lambda^2\,\int_0^t d\tau\;\sin\Delta\tau\;\mathrm{Re}\,C(\tau)\;, \end{cases} \tag{43}$$

with the bath correlation function (16)

$$C(\tau) \equiv \mathrm{tr}_{\rm b}\,\rho_{\rm b}^{\rm eq}\,\exp(iH_{\rm b}\tau)\,B\,\exp(-iH_{\rm b}\tau)\,B \tag{44}$$

$$= \int_0^\infty d\omega\,J(\omega)\,\left(\coth\frac{\beta\omega}{2}\,\cos\omega\tau - i\,\sin\omega\tau\right)\;. \tag{45}$$

We remark that the bath correlation function decays asymptotically fast enough, such as $\mathrm{Re}\,C(\tau) \sim \tau^{-4}$ and $\mathrm{Im}\,C(\tau) \sim \tau^{-5}$ for $\tau \to \infty$. Accordingly, the time integrals which define the slippage superoperator (25) converge for this model. This slippage superoperator is here given by

$$\begin{cases} x^{\rm R}(0) = \left[1 + \dfrac{s_g}{2} - \dfrac{h(\infty)}{2\Delta}\right]\,x(0) - \dfrac{s_h}{2}\,y(0)\;, \\[2mm] y^{\rm R}(0) = \dfrac{s_h}{2}\,x(0) + \left[1 + \dfrac{s_g}{2} + \dfrac{h(\infty)}{2\Delta}\right]\,y(0)\;, \\[2mm] z^{\rm R}(0) = s_f + (1 + s_g)\,z(0)\;, \end{cases} \tag{46}$$
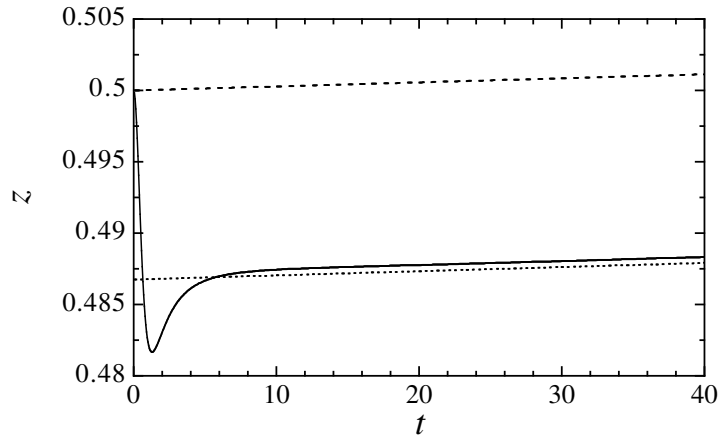
FIG. 3: Short-time dynamics of the population variable $z(t)$ for the spin-boson model with $\lambda = 0.1$, $\Delta = 0.1$, $\omega_c = 1$, $T = 0$, as obtained by different approximations: the non-Markovian equations (42) (solid line); the non-slipped Redfield equations (48) (long-dashed line); the Redfield equations (48) from initial conditions slipped by our slippage transformation (46) (short-dashed line).

with the coefficients

$$\begin{cases} s_f = 4\,\lambda^2 \int_0^\infty d\tau\,\tau\,\sin\Delta\tau\,\operatorname{Im} C(\tau)\,, \\ s_g = 4\,\lambda^2 \int_0^\infty d\tau\,\tau\,\cos\Delta\tau\,\operatorname{Re} C(\tau)\,, \\ s_h = 4\,\lambda^2 \int_0^\infty d\tau\,\tau\,\sin\Delta\tau\,\operatorname{Re} C(\tau)\,, \end{cases} \tag{47}$$

and $h(\infty) = \lim_{t\to\infty} h(t)$ for the function $h(t)$ in Eq. (43).

After the slippage of initial conditions which transforms $[x(0), y(0), z(0)]$ into $[x^R(0), y^R(0), z^R(0)]$, the dynamics may be approximated by the Redfield master equation for times $t \gg t_b \sim 1/\omega_c$. The Markovian equation is obtained by replacing the time t by infinity in the coefficients (43) of the non-Markovian equation (42), leading to the Redfield equations

$$\begin{cases} \dot{x}^R = \Delta\,y^R\,, \\ \dot{y}^R = -[\Delta + h(\infty)]\,x^R - g(\infty)\,y^R\,, \\ \dot{z}^R = -f(\infty) - g(\infty)\,z^R\,. \end{cases} \tag{48}$$

Following Suarez et al. [10], we consider that the bath is at zero temperature $T = 0$, and that the parameters of the model take the values $\lambda = 0.1$, $\Delta = 0.1$, and $\omega_c = 1$. The initial conditions are chosen at the point $[x(0) = 0, y(0) = \sqrt{3}/2, z(0) = 1/2]$ on the surface of the Bloch unit sphere, i.e., on the border between the admissible and non-admissible density matrices. The coefficients for the Redfield equations (48) and the slippage superoperator (46) can be computed by numerical integration.

We have compared the short-time dynamics of the non-Markovian master equations (42) with that of the Redfield equations (48) for both non-slipped and slipped initial conditions. The short-time dynamics of the population variable $z(t)$ is depicted in Fig. 3, while the determinant (41) is depicted in Fig. 4.

Figure 4 shows that the Redfield equations violate positivity if the initial conditions are not slipped. In contrast, the non-Markovian equations (42) brings the trajectory well inside the set of admissible density matrices on a short time of the order of the bath relaxation time $t_b \sim 1/\omega_c$, as already observed by Suarez et al. [10]. The new result is that our slippage superoperator (46) has the proper effect of slipping the initial conditions by an amount which agrees with the non-Markovian dynamics given by Eqs. (42) at the second order of perturbation theory.

In this regard, we should notice that the slippage (25) or (46) is calculated by series expansion up to second order in the coupling parameter λ, which explains the small remaining difference between the trajectory of the Redfield equations for slipped initial conditions and that of the non-Markovian equations (42), as seen in Figs. 3 and 4. A refined slippage could be obtained by complete integration of the linear equations (42) and (48) and by calculating the slippage at all orders in the coupling parameter λ. However, since the non-Markovian master equations (42) are only valid at second order, such a refined slippage would remain limited in any case to the second-order perturbation theory. Therefore, the small remaining difference between both trajectories should be attributed to corrections of higher orders in λ than the second order.
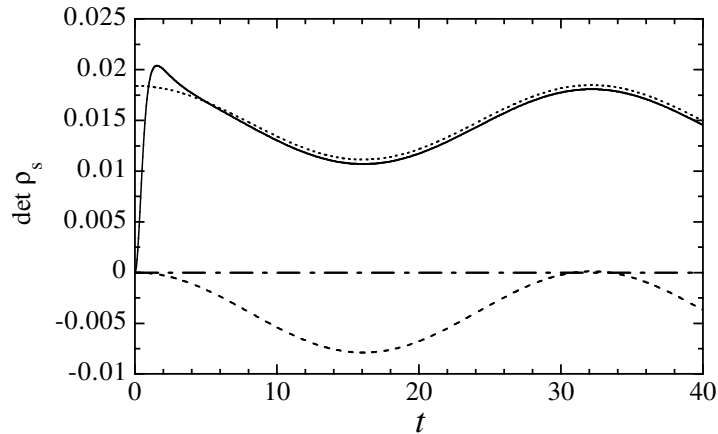
FIG. 4: Short-time dynamics of the determinant (41) of the reduced density matrix of the spin-boson model under the same conditions as in Fig. 3. The dotted-dashed line is the separatrix $\det \rho_s = 0$ between the admissible density matrices for which $\det \rho_s \geq 0$, and the non-admissible ones. The different lines correspond to those of Fig. 3.

Consequently, we have shown that the agreement between the non-Markovian dynamics and its Markovian approximation can be improved significantly if the Redfield time evolution starts from initial conditions which are slipped by our superoperator (25), validating the proposition (22).

Furthermore, we have also tested whether positivity is still violated after slippage. For the non-slipped Redfield equations, we have numerically checked that a majority of initial conditions taken on the surface of the Bloch unit sphere generate a trajectory which violates positivity over a given time interval $0 \leq t < 40$, as previously observed. However, when the same initial conditions are mapped inside the Bloch unit sphere by our slippage transformation (46), *none* of the trajectories generated with the Redfield equations for these slipped initial conditions has been observed to violate positivity over the same time interval. In conclusion, this observation indicates that the problem of the violation of positivity by the Redfield equations can be solved by our slippage superoperator (25).

VI. CONCLUSIONS

In this paper, we have derived the general form (25) of the slippage of initial conditions that describes the fast dynamics in the early stage of the time evolution of a subsystem coupled to a thermal bath. The slippage should preserve both Hermiticity and normalization. It is of second order in the coupling parameter and finds its origin in the relaxation of the bath coupling operators over a short but non-vanishing time t_b, which explains that the slippage is proportional to this bath relaxation time t_b. Accordingly, for δ-correlated baths, the slippage superoperator (25) becomes the identity, meaning that no slippage is required. In this regard, the slippage takes into account the memory effect of the initial condition which arises in general due to the non-Markovian character of the basic master equation (14).

Moreover, our slippage superoperator improves considerably the agreement between the approximate and the exact time dynamics, as we have shown for the example of the spin-boson model. We have also shown on this example that our slippage superoperator brings about the initial reduced density matrix sufficiently inside the set of physically admissible density matrices in order for positivity to be preserved during a subsequent time evolution under the Redfield master equation.

We can therefore conclude that memory effects in the short-time dynamics of a slow quantum subsystem weakly coupled to a fast reservoir can be taken into account by introducing a slippage superoperator before the time dynamics of the Markovian Redfield equation starts, as summarized by Eq. (22).

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APPENDIX A

The potential (2) can be written as a sum of Hermitian subsystem and bath operators redefined as follows

$$S'_\alpha \;\; = \; + \; \tfrac{1}{2}(S_\alpha + S_\alpha^\dagger) \;, \qquad S''_\alpha \; = \; + \; \tfrac{i}{2}(S_\alpha - S_\alpha^\dagger) \;, \tag{49}$$

$$B'_\alpha \;\; = \; + \; \tfrac{1}{2}(B_\alpha + B_\alpha^\dagger) \;, \qquad B''_\alpha \; = \; - \; \tfrac{i}{2}(B_\alpha - B_\alpha^\dagger) \;, \tag{50}$$

so that the potential becomes

$$V \; = \; \sum_\alpha \; (S'_\alpha \, B'_\alpha \; + \; S''_\alpha \, B''_\alpha) \;. \tag{51}$$

For Hermitian bath coupling operators, the bath correlation functions (16) have the property

$$C_{\alpha\beta}^*(\tau) \; = \; C_{\beta\alpha}(-\tau) \;. \tag{52}$$

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[1] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[2] P. Résibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).
[3] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977).
[4] N. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992) 2nd edition.
[5] W. Pauli, *Festschrift zum 60. Geburtstage A. Sommerfelds* (Hirzel, Leipzig, 1928) p. 30.
[6] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[7] M. B. Plenio and P. L. Knight, Rev. Mod. Phys. **70**, 101 (1998).
[8] A. G. Redfield, IBM J. Research Devel. **1**, 19 (1957); A. G. Redfield, Adv. Magn. Reson. **1**, 1 (1965).
[9] R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications* (Springer, Berlin, 1987).
[10] A. Suárez, R. Silbey, and I. Oppenheim, J. Chem. Phys. **97**, 5101 (1992).
[11] P. Pechukas, Phys. Rev. Lett. **73**, 1060 (1994).
[12] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[13] W. T. Pollard and R. A. Friesner, J. Chem. Phys. **100**, 5054 (1994).
[14] I. Prigogine, in: S. Claesson, Editor, *Fast Reactions and Primary Processes in Chemical Kinetics*, Proceedings of the Nobel Symposium 5 (Almqvist & Wiksell, Stockholm; and Wiley-Interscience, New York; 1967) pp. 99-129; Cl. George, Physica **37**, 182 (1967); R. Balescu and J. Wallenborn, Physica **54**, 477 (1971); R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975) p. 556.