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Quantum master equation for a system influencing its environment

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A perturbative quantum master equation is derived for a system interacting with its environment, which is more general than the ones derived before. Our master equation takes into account the effect of the energy exchanges between the system and the environment and the conservation of energy in the finite total system. This master equation describes relaxation mechanisms in isolated nanoscopic quantum systems. In its most general form, this equation is non-Markovian and a Markovian version of it rules the long-time relaxation. We show that our equation reduces to the Redfield equation in the limit where the energy of the system does not affect the density of state of its environment. This master equation and the Redfield one are applied to a spin-environment model defined in terms of random matrices and compared with the solutions of the exact von Neumann equation. The comparison proves the necessity to allow energy exchange between the subsystem and the environment in order to correctly describe the relaxation in an isolated nanoscopic total system.

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I. INTRODUCTION

Studying the dynamics of a simple system interacting with its environment is a very important problem in physics. The theoretical description of this problem started a long time ago.

In the context of classical mechanics several master equations, such as the Boltzmann equation, the Chapman-Kolmogorov master equation, or the Fokker-Planck equation, were derived in order to describe the time evolution of the probability density of the system variables.

In the context of quantum mechanics, which interests us in this paper, the time evolution of a system interacting with its environment is described in terms of a reduced density matrix that is obtained by tracing out the degrees of freedom of the environment from the total (system plus environment) density matrix. In this way, the first quantum master equation was obtained by Pauli [1–3] in 1928. This equation is called the *Pauli equation* and describes the evolution of the populations (i.e., the diagonal elements of the density matrix) when the system is weakly perturbed by an additional term in its Hamiltonian. The transition rates between populations are given by the Fermi golden rule. In 1957, Redfield [4] derived the so-called *Redfield equation* in the context of NMR for a system such as a spin interacting with its environment. This equation has been widely used and applied to many systems where the dynamics of the environment is faster than the dynamics of the system. This equation is Markovian and has the defect of breaking the positivity on short time scales of the order of the environment correlation time for initial conditions near the border of the space of physically admissible density matrices. Many similar master equations for a system interacting with an environment have been derived since then starting from the von Neumann equation and making several assumptions (weak coupling limit, Markovianity, separation of time scale between system and environment) [5–9]. In 1976 Lindblad [10] derived the most general quantum master equation which is Markovian and which preserves positivity. The Redfield equation has a Lindblad form in the case of δ-correlated environments. More recently, a *non-Markovian Redfield equation* has been obtained that preserves positivity and reduces to the Redfield equation in the Markovian limit [11]. It has also been shown [11,12] that the Markovian Redfield equation can preserve positivity if one applies a slippage of initial conditions that takes into account the non-Markovian effects on the early dynamics. Similar considerations have been proposed for different master equations [13–15]. As far as one considers the weak-coupling regime, all the master equations derived till now in the literature at second order of perturbation theory can be deduced from the non-Markovian Redfield equation.

The problem is that the non-Markovian Redfield equation as well as the other aforementioned master equations existing in the literature are based on the fundamental assumption that the environment does not feel the effect of the system. This assumption seems realistic for macroscopic environments but not in the case of nanoscopic isolated total systems in which the density of states of the environment can vary on an energy scale of the order of the system energy scale. Because nanoscopic physics is experimentally progressing very fast, we expect that such effects will become important and measurable in future applications. Already, quantum dissipation is being envisaged on the nanoscale for applications such as spin dynamics in quantum dots [16] or isomerizations in atomic or molecular clusters in microcanonical statistical ensembles [17]. Another possible application is the intramolecular energy relaxation in polyatomic molecules [18].

The aim of the present paper is to systematically derive from the von Neumann equation a master equation which takes into account the fact that the energy of the total system (system plus environment) is finite and constant and, therefore, that the energy distribution of the environment is affected by energy exchanges with the system. The aforementioned equations can be derived from our master equation, which thus appears to be very general.

The plan of the paper is the following. In Sec. II we systematically derive our master equation and the non-

Markovian Redfield equation from the von Neumann equation, by performing a second-order perturbative expansion in the coupling parameter (under the assumption of weak coupling) for general environments. Thereafter, we consider the Markovian limit in both cases. We also show how, in this limit and neglecting the coupling between the populations and the quantum coherences, our master equation reduces to a simple equation of Pauli type for the total system, taking into account the modifications of the energy distribution of the environment due to the energy exchanges with the system. Finally, we compare our master equation to the Redfield equation and discuss how the Redfield equation can be seen as a particular case of our master equation. In Sec. III we apply our master equation and the Redfield equation to the case where the system is a two-level system interacting with a general environment. In Sec. IV we apply the master equations to the case where the system is a two-level system interacting with a complex environment (such as a classically chaotic or many-body environment) that is modeled by random matrices from a Gaussian orthogonal ensemble, which we call Gaussian orthogonal random matrices (GORM). In Sec. V, we compare the solutions of the non-Markovian and Markovian master equations to the exact solutions of the complete von Neumann equation in the case of our spin-GORM model. Conclusions are finally drawn in Sec. VI.

II. DERIVATION OF THE FUNDAMENTAL EQUATIONS

The Hamiltonian of the total systems that we consider here is made of the sum of the system Hamiltonian $\hat{H}_S$ and the environment Hamiltonian $\hat{H}_B$ plus a coupling term that has the form of the product of a system operator $\hat{S}$ and a environment operator $\hat{B}$. The generalization to a coupling term of the form $\lambda \Sigma_i \hat{S}_i \hat{B}_i$ is easy. The amplitude of the coupling term is determined by the coupling parameter λ:

$$\hat{H}_{\text{tot}} = \hat{H}_0 + \lambda \hat{V} = \hat{H}_S + \hat{H}_B + \lambda \hat{S}\hat{B}. \tag{1}$$

The eigenstates of $\hat{H}_S$, respectively of $\hat{H}_B$, will be denoted by $|s\rangle$, respectively $|b\rangle$. The eigenvalues of $\hat{H}_S$, respectively of $\hat{H}_B$, will be denoted by E_s, respectively E_b. Finally, the eigenstates of $\hat{H}_{\text{tot}}$ will be denoted by $|\alpha\rangle$ and its eigenvalues by E_α.

The evolution of the total density matrix is described by the von Neumann equation:

$$\dot{\hat{\rho}}(t) = -i[\hat{H}_{\text{tot}}, \hat{\rho}(t)] \equiv \mathcal{L}_{\text{tot}} \hat{\rho}(t), \tag{2}$$

where $\mathcal{L}_{\text{tot}}$ is the so-called quantum Liouvillian or von Neumann operator of the total system. The interaction representations of the operators are given by

$$\begin{aligned}
\hat{\rho}_I(t) &= e^{i\hat{H}_0 t} \hat{\rho}(t) e^{-i\hat{H}_0 t},\\
\hat{V}(t) &= e^{i\hat{H}_0 t} \hat{V} e^{-i\hat{H}_0 t},\\
\hat{B}(t) &= e^{i\hat{H}_B t} \hat{B} e^{-i\hat{H}_B t},\\
\hat{S}(t) &= e^{i\hat{H}_S t} \hat{S} e^{-i\hat{H}_S t}.
\end{aligned} \tag{3}$$

In the interaction representation, the von Neumann equation becomes

$$\dot{\hat{\rho}}_I(t) = -i[\lambda \hat{V}(t), \hat{\rho}_I(t)] \equiv \mathcal{L}_I(t) \hat{\rho}_I(t), \tag{4}$$

with the interaction Liouvillian $\mathcal{L}_I(t) = e^{-\mathcal{L}_0 t} \mathcal{L}_I e^{\mathcal{L}_0 t}$ where $e^{\mathcal{L}_0 t}\hat{A} = e^{-i\hat{H}_0 t} \hat{A} e^{i\hat{H}_0 t}$, the free Liouvillian $\mathcal{L}_0 = \mathcal{L}_S + \mathcal{L}_B = -i[\hat{H}_S, \cdot] - i[\hat{H}_B, \cdot]$, and $\hat{A}$ is an arbitrary operator. The perturbative expression of the von Neumann equation in the interaction representation is given to order λ^2 by

$$\begin{aligned}
\hat{\rho}_I(t) &= \hat{\rho}(0) + \int_0^t dt_1 \mathcal{L}_I(t_1) \hat{\rho}(0)\\
&\quad + \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{L}_I(t_1) \mathcal{L}_I(t_2) \hat{\rho}(0) + O(\lambda^3)
\end{aligned} \tag{5}$$

$$\begin{aligned}
&= \hat{\rho}(0) + \int_0^t dT e^{-\mathcal{L}_0 T} \mathcal{L}_I e^{\mathcal{L}_0 T} \hat{\rho}(0)\\
&\quad + \int_0^t dT \int_0^T d\tau e^{-\mathcal{L}_0 T} \mathcal{L}_I e^{\mathcal{L}_0 \tau} \mathcal{L}_I e^{-\mathcal{L}_0 \tau} e^{\mathcal{L}_0 T} \hat{\rho}(0)\\
&\quad + O(\lambda^3),
\end{aligned} \tag{6}$$

if we set $T = t_1$ and $\tau = t_1 - t_2$. Equation (6) is the starting point of all the derivations of a master equation in the weak coupling limit for a total system made of a system and its environment in mutual interaction.

A. Our quantum master equation

We now derive our master equation which is the central result of this paper. The main idea is to describe the time evolution in terms of quantities which are distributed over the energy of the environment. We thus define the following quantities in terms of which we intend to describe the properties of the system:

$$P_{ss'}(\epsilon;t) \equiv \text{Tr}\, \hat{\rho}(t) |s'\rangle\langle s| \delta(\epsilon - \hat{H}_B). \tag{7}$$

The diagonal element $P_{ss}(\epsilon;t)$ is the probability density to find the system in the state s while the environment has the energy ϵ. The off-diagonal element $P_{ss'}(\epsilon;t)$ characterizes the density of the quantum coherence between the states s and s', density which is distributed over the energy ϵ of the environment.

The matrix composed of the elements $P_{ss'}(\epsilon;t)$ is Hermitian

$$P_{ss'}(\epsilon;t) = P^*_{s's}(\epsilon;t). \tag{8}$$

Moreover, the normalization $\mathrm{Tr}\,\hat{\rho}(t)=1$ of the total density matrix implies that

$$\sum_{s} \int d\epsilon\, P_{ss}(\epsilon;t)=1. \tag{9}$$

In order to obtain a closed description in terms of the quantities (7), we suppose that the total density matrix can be described at all times by a density matrix of the following form:

$$\hat{\rho}(t)=\sum_{s,s'} |s\rangle\langle s'| \frac{P_{ss'}(\hat{H}_B;t)}{n(\hat{H}_B)}, \tag{10}$$

where we have defined the energy density

$$n(\epsilon)=\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B), \tag{11}$$

which is supposed to be smoothened on the energy scale of the mean level spacing. The assumption (10) has the effect of neglecting the contributions from the environment coherences to the system dynamics (albeit the system coherences are kept in the description). We remark that the form (10) is not supposed to strictly hold at all times but is an assumption in order to obtain a closed set of equations for the quantities $P_{ss'}(\epsilon;t)$.

In order to better understand the meaning of the above definitions, we notice that the reduced density matrix of the system takes the form

$$\hat{\rho}_S(t)=\mathrm{Tr}_B\hat{\rho}(t)=\int d\epsilon\, \mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{\rho}(t)$$

$$=\int d\epsilon \sum_{s,s'} |s\rangle P_{ss'}(\epsilon;t)\langle s'|, \tag{12}$$

which can be represented in the basis of the eigenstates of the system Hamiltonian as

$$\hat{\rho}_S(t)=\int d\epsilon \begin{pmatrix} P_{11}(\epsilon;t) & P_{12}(\epsilon;t) & \dots & P_{1N_S}(\epsilon;t) \\ P_{21}(\epsilon;t) & P_{22}(\epsilon;t) & \dots & P_{2N_S}(\epsilon;t) \\ \vdots & \vdots & \ddots & \vdots \\ P_{N_S1}(\epsilon;t) & P_{N_S2}(\epsilon;t) & \dots & P_{N_SN_S}(\epsilon;t) \end{pmatrix}. \tag{13}$$

The goal of the precedent choice for the form of $\hat{\rho}(t)$ is thus to obtain a description in which the state s of the system is correlated with the energy ϵ of the environment. In other words, the density matrix $\hat{\rho}_S$ of the system is decomposed as a distribution over the energy ϵ of the environment.

We now proceed to the derivation of the equations of motion for our quantities $P_{ss'}(\epsilon;t)$ in the weak-coupling limit. We start from the perturbative expansion (6) of the total density matrix in the interaction representation (3). We first define the interaction representation of our quantities (7):

$$P_{Iss'}(\epsilon;t)=e^{i(E_s-E_{s'})t}P_{ss'}(\epsilon;t). \tag{14}$$

We now have that

$$P_{Iss'}(\epsilon;t)=\mathrm{Tr}\,\hat{\rho}_I(t)|s'\rangle\langle s|\,\delta(\epsilon-\hat{H}_B). \tag{15}$$

Inserting the perturbative expansion (6), we get

$$\begin{aligned} P_{Iss'}(\epsilon;t)=&\,\mathrm{Tr}\,\hat{X}\hat{\rho}(0)+\int_0^t dT\,\mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0T}\mathcal{L}_Ie^{\mathcal{L}_0T}\hat{\rho}(0)\\ &+\int_0^t dT\int_0^T d\tau\,\mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0T}\\ &\times\mathcal{L}_Ie^{\mathcal{L}_0\tau}\mathcal{L}_Ie^{-\mathcal{L}_0\tau}e^{\mathcal{L}_0T}\hat{\rho}(0)+O(\lambda^3), \end{aligned} \tag{16}$$

where $\hat{X}=|s'\rangle\langle s|\,\delta(\epsilon-\hat{H}_B)$. Differentiating with respect to time, we obtain the equation

$$\begin{aligned} \dot{P}_{Iss'}(\epsilon;t)=&\,\mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0t}\mathcal{L}_Ie^{\mathcal{L}_0t}\hat{\rho}(0)\\ &+\int_0^t d\tau\,\mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0t}\mathcal{L}_Ie^{\mathcal{L}_0\tau}\mathcal{L}_Ie^{-\mathcal{L}_0\tau}e^{\mathcal{L}_0t}\hat{\rho}(0)\\ &+O(\lambda^3), \end{aligned} \tag{17}$$

where the initial density matrix takes the assumed form (10) with $t=0$.

The first term is thus explicitly given by

$$\begin{aligned} \mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0t}\mathcal{L}_Ie^{\mathcal{L}_0t}\hat{\rho}(0)=&-i\lambda\,\mathrm{Tr}|s'\rangle\langle s|\,\delta(\epsilon-\hat{H}_B)e^{i\hat{H}_0t}\\ &\times[\hat{V},e^{-i\hat{H}_0t}\hat{\rho}(0)e^{i\hat{H}_0t}]e^{-i\hat{H}_0t}\\ =&-i\lambda\sum_{\bar{s}} e^{i(E_s-E_{\bar{s}})t}\langle s|\hat{S}|\bar{s}\rangle\\ &\times P_{\bar{s}s'}(\epsilon;0)n(\epsilon)\langle\hat{B}\rangle_\epsilon\\ &+i\lambda\sum_{\bar{s}} e^{-i(E_{s'}-E_{\bar{s}})t}\langle\bar{s}|\hat{S}|s'\rangle\\ &\times P_{s\bar{s}}(\epsilon;0)n(\epsilon)\langle\hat{B}\rangle_\epsilon, \end{aligned} \tag{18}$$

with the environment coupling operator $\hat{B}$ averaged over the microcanonical state of the environment

$$\langle\hat{B}\rangle_\epsilon\equiv\frac{\mathrm{Tr}\,\delta(\epsilon-\hat{H}_B)\hat{B}}{n(\epsilon)}. \tag{19}$$

We now assume that this average vanishes, $\langle B\rangle_\epsilon=0$. Otherwise, the nonvanishing average is absorbed in the system Hamiltonian by the following substitutions:

$$\hat{H}_S\rightarrow\hat{H}_S+\lambda\langle\hat{B}\rangle_\epsilon\hat{S}, \tag{20}$$

$$\hat{V}\rightarrow\hat{V}-\langle\hat{B}\rangle_\epsilon\hat{S}, \tag{21}$$

$$\hat{H}_B\rightarrow\hat{H}_B, \tag{22}$$

leaving unchanged the total Hamiltonian. Thanks to this simplification, the first-order term of the perturbative expansion vanishes

$$\mathrm{Tr}\,\hat{X} e^{-\mathcal{L}_0 t}\mathcal{L}_I e^{\mathcal{L}_0 t}\hat{\rho}(0)=0. \tag{23}$$

As a consequence, the time evolution of the total density matrix is given by the uncoupled Hamiltonian $\hat{H}_0=\hat{H}_S+\hat{H}_B$ up to correction of the order of λ^2:

$$\hat{\rho}(t)=e^{\mathcal{L}_0 t}\hat{\rho}(0)+O(\lambda^2). \tag{24}$$

According to our closure assumption that the total density matrix keeps the form (10) during its time evolution, we have that

$$e^{\mathcal{L}_0 t}\hat{\rho}(0)=\hat{\rho}(t)+O(\lambda^2)=\sum_{\overline{s},\overline{s}'}|\overline{s}\rangle\langle\overline{s}'|\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}+O(\lambda^2), \tag{25}$$

which we can substitute in Eq. (17) to get

$$\begin{aligned}\dot{P}_{Iss'}(\epsilon;t)&=\int_0^t d\tau\,\mathrm{Tr}\,\hat{X}e^{-\mathcal{L}_0 t}\mathcal{L}_I e^{\mathcal{L}_0 \tau}\mathcal{L}_I e^{-\mathcal{L}_0 \tau}e^{\mathcal{L}_0 t}\hat{\rho}(0)\\&\quad+O(\lambda^3)\\&=-\lambda^2 e^{i(E_s-E_{s'})t}\sum_{\overline{s},\overline{s}'}\int_0^t d\tau\,\mathrm{Tr}\Big\{|s'\rangle\langle s|\delta(\epsilon-\hat{H}_B)\\&\quad\times\Big[\hat{S}\hat{B},\Big[\hat{S}(-\tau)\hat{B}(-\tau),|\overline{s}\rangle\langle\overline{s}'|\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\Big]\Big]\Big\}\\&\quad+O(\lambda^3).\end{aligned} \tag{26}$$

Going back to the original representation with Eq. (14) and expanding the two commutators, we obtain

$$\begin{aligned}\dot{P}_{ss'}(\epsilon;t)={}&-i(E_s-E_{s'})P_{ss'}(\epsilon;t)-\lambda^2\sum_{\overline{s},\overline{s}'}\int_0^t d\tau\Big\{\langle s|\hat{S}\hat{S}(-\tau)|\overline{s}\rangle\langle\overline{s}'|s'\rangle\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}\hat{B}(-\tau)\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\\&-\langle s|\hat{S}|\overline{s}\rangle\langle\overline{s}'|\hat{S}(-\tau)|s'\rangle\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}(-\tau)-\langle s|\hat{S}(-\tau)|\overline{s}\rangle\langle\overline{s}'|\hat{S}|s'\rangle\\&\times\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}(-\tau)\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}+\langle s|\overline{s}\rangle\langle\overline{s}'|\hat{S}(-\tau)\hat{S}|s'\rangle\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}(-\tau)\hat{B}\Big\}+O(\lambda^3).\end{aligned} \tag{27}$$

In order to evaluate the four last terms, we notice that, for a quasicontinuous energy spectrum, we can write

$$\begin{aligned}&\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}\,\delta(\epsilon'-\hat{H}_B)\hat{B}\\&\quad=\sum_{b,b'}\delta(\epsilon-E_b)\,\delta(\epsilon'-E_{b'})|\langle b|\hat{B}|b'\rangle|^2\\&\quad=n(\epsilon)n(\epsilon')F(\epsilon,\epsilon'),\end{aligned} \tag{28}$$

where the function $F(\epsilon,\epsilon')$ stands for

$$F(\epsilon,\epsilon')\equiv\text{``}|\langle\epsilon|\hat{B}|\epsilon'\rangle|^2\text{''}, \tag{29}$$

where $|\epsilon\rangle$ denotes the eigenstate $|b\rangle$ of the environment Hamiltonian $\hat{H}_B$ corresponding to the energy eigenvalue $E_b=\epsilon$. Equation (29) supposes some smoothening of the squares $|\langle\epsilon|\hat{B}|\epsilon'\rangle|^2$ of the matrix elements of $\hat{B}$ over a dense spectrum of eigenvalues around the energies ϵ and ϵ'. The function (29) has the symmetry

$$F(\epsilon,\epsilon')=F(\epsilon',\epsilon). \tag{30}$$

With the definition (29) and the identity

$$\int d\epsilon'\,\delta(\epsilon'-\hat{H}_B)=\hat{I}, \tag{31}$$

we can now write that

$$\begin{aligned}&\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}\hat{B}(-\tau)\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\\&\quad=P_{\overline{s}\overline{s}'}(\epsilon;t)\int d\epsilon'\,n(\epsilon')F(\epsilon,\epsilon')e^{+i(\epsilon-\epsilon')t},\end{aligned} \tag{32}$$

$$\begin{aligned}&\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}(-\tau)\\&\quad=n(\epsilon)\int d\epsilon'\,P_{\overline{s}\overline{s}'}(\epsilon';t)F(\epsilon,\epsilon')e^{+i(\epsilon-\epsilon')t},\end{aligned} \tag{33}$$

$$\begin{aligned}&\mathrm{Tr}_B\delta(\epsilon-\hat{H}_B)\hat{B}(-\tau)\frac{P_{\overline{s}\overline{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}\\&\quad=n(\epsilon)\int d\epsilon'\,P_{\overline{s}\overline{s}'}(\epsilon';t)F(\epsilon,\epsilon')e^{-i(\epsilon-\epsilon')t},\end{aligned} \tag{34}$$

$$\mathrm{Tr}_B\,\delta(\epsilon-\hat{H}_B)\frac{P_{\bar{s}\bar{s}'}(\hat{H}_B;t)}{n(\hat{H}_B)}\hat{B}(-\tau)\hat{B} = P_{\bar{s}\bar{s}'}(\epsilon;t)\int d\epsilon'\,n(\epsilon')F(\epsilon,\epsilon')e^{-i(\epsilon-\epsilon')t}. \tag{35}$$

Accordingly, our quantum master equation finally takes the closed form

$$\begin{aligned}\dot{P}_{ss'}(\epsilon;t) = {} & -i(E_s-E_{s'})P_{ss'}(\epsilon;t)-\lambda^2\sum_{\bar{s},\bar{s}'}\int d\epsilon'\,F(\epsilon,\epsilon')\\ & \times\int_0^t d\tau\{\langle s|\hat{S}|\bar{s}'\rangle\langle\bar{s}'|\hat{S}|\bar{s}\rangle P_{\bar{s}s'}(\epsilon;t)n(\epsilon')\\ & \times e^{+i(\epsilon-\epsilon'+E_{\bar{s}}-E_{\bar{s}'})\tau}-\langle s|\hat{S}|\bar{s}\rangle\langle\bar{s}'|\hat{S}|s'\rangle\\ & \times P_{\bar{s}\bar{s}'}(\epsilon';t)n(\epsilon)e^{+i(\epsilon-\epsilon'+E_{s'}-E_{\bar{s}'})\tau}-\langle s|\hat{S}|\bar{s}\rangle\\ & \times\langle\bar{s}'|\hat{S}|s'\rangle P_{\bar{s}\bar{s}'}(\epsilon';t)n(\epsilon)e^{-i(\epsilon-\epsilon'+E_s-E_{\bar{s}})\tau}\\ & +\langle\bar{s}'|\hat{S}|\bar{s}\rangle\langle\bar{s}|\hat{S}|s'\rangle P_{s\bar{s}'}(\epsilon;t)n(\epsilon')\\ & \times e^{-i(\epsilon-\epsilon'+E_{\bar{s}'}-E_{\bar{s}})\tau}\}+\mathcal{O}(\lambda^3).\end{aligned} \tag{36}$$

Equation (36) determines the time evolution of the distribution functions $P_{ss'}(\epsilon;t)$ describing the populations and quantum coherences of a system influencing its environment and is the central result of this paper. It is a non-Markovian equation because of the presence of the time integral in the right-hand side.

In Eq. (36) the function $n(\epsilon)F(\epsilon,\epsilon')$ determines the properties of the coupling to the environment and, in particular, the time scale of the environment. If this time scale is supposed to be shorter then the system time scales $\{2\pi/(E_s-E_{s'})\}$, we can perform a *Markovian approximation* in Eq. (36). Such an approximation is justified for a process evolving on time scales larger than the environment time scale. The Markovian approximation consists in taking the limit where the upper bound of the time integral goes to infinity and using the following relations:

$$\int_0^\infty d\tau\,e^{\pm i\omega\tau}=\pm i\mathrm{P}\frac{1}{\omega}+\pi\delta(\omega), \tag{37}$$

where P denotes the principal part.

We finally obtain the Markovian version of our quantum master equation (36) as

$$\begin{aligned}\dot{P}_{ss'}(\epsilon;t) = {} & -i(E_s-E_{s'})P_{ss'}(\epsilon;t)-i\lambda^2\sum_{\bar{s},\bar{s}'}\left\{\left[\int d\epsilon'\,n(\epsilon')F(\epsilon,\epsilon')\mathrm{P}\frac{1}{\epsilon-\epsilon'+E_{\bar{s}}-E_{\bar{s}'}}\right]\right.\\ & \times[\langle s|\hat{S}|\bar{s}'\rangle\langle\bar{s}'|\hat{S}|\bar{s}\rangle P_{\bar{s}s'}(\epsilon;t)-\langle\bar{s}|\hat{S}|\bar{s}'\rangle\langle\bar{s}'|\hat{S}|s'\rangle P_{s\bar{s}}(\epsilon;t)]-\langle s|\hat{S}|\bar{s}\rangle\langle\bar{s}'|\hat{S}|s'\rangle n(\epsilon)\int d\epsilon'\,F(\epsilon,\epsilon')P_{\bar{s}\bar{s}'}(\epsilon';t)\\ & \left.\times\left[\mathrm{P}\frac{1}{\epsilon-\epsilon'+E_{s'}-E_{\bar{s}'}}-\mathrm{P}\frac{1}{\epsilon-\epsilon'+E_s-E_{\bar{s}}}\right]\right\}-\pi\lambda^2\sum_{\bar{s},\bar{s}'}\{n(\epsilon+E_{\bar{s}}-E_{\bar{s}'})F(\epsilon,\epsilon+E_{\bar{s}}-E_{\bar{s}'})\\ & \times[\langle s|\hat{S}|\bar{s}'\rangle\langle\bar{s}'|\hat{S}|\bar{s}\rangle P_{\bar{s}s'}(\epsilon;t)+\langle\bar{s}|\hat{S}|\bar{s}'\rangle\langle\bar{s}'|\hat{S}|s'\rangle P_{s\bar{s}}(\epsilon;t)]-\langle s|\hat{S}|\bar{s}\rangle\langle\bar{s}'|\hat{S}|s'\rangle n(\epsilon)\\ & \times[F(\epsilon,\epsilon+E_{s'}-E_{\bar{s}'})P_{\bar{s}\bar{s}'}(\epsilon+E_{s'}-E_{\bar{s}'};t)+F(\epsilon,\epsilon+E_s-E_{\bar{s}})P_{\bar{s}\bar{s}'}(\epsilon+E_s-E_{\bar{s}};t)]\}+O(\lambda^3).\end{aligned} \tag{38}$$

We notice that the use of this Markovian equation may require a slippage of initial conditions as shown in Refs. [11,12]. In Eq. (38), the last terms in $\pi\lambda^2$ typically describe the relaxation to a stationary solution. The terms in $i\lambda^2$ modify the frequencies of oscillations and include the so-called Lamb shifts of the zeroth-order energy eigenvalues. Indeed, if we consider only the evolution of the off-diagonal matrix element $P_{ss'}(\epsilon;t)$ by neglecting its coupling to all the other matrix elements, we obtain the equation

$$\dot{P}_{ss'}(\epsilon;t)\simeq\{-i[\tilde{E}_s(\epsilon)-\tilde{E}_{s'}(\epsilon)]-\Gamma_{ss'}(\epsilon)\}P_{ss'}(\epsilon;t), \tag{39}$$

with the energies modified by the Lamb shifts

$$\begin{aligned}\tilde{E}_s(\epsilon) = {} & E_s+\lambda^2\sum_{\bar{s}}|\langle s|\hat{S}|\bar{s}\rangle|^2\int d\epsilon'\,n(\epsilon')F(\epsilon,\epsilon')\\ & \times\mathrm{P}\frac{1}{\epsilon-\epsilon'+E_s-E_{\bar{s}}}+O(\lambda^3)\end{aligned} \tag{40}$$

and the damping rates

$$\begin{aligned}\Gamma_{ss'}(\epsilon) = {} & \pi\lambda^2\sum_{\bar{s}(\neq s)}[|\langle s|\hat{S}|\bar{s}\rangle|^2 n(\epsilon+E_s-E_{\bar{s}})\\ & \times F(\epsilon,\epsilon+E_s-E_{\bar{s}})+|\langle s'|\hat{S}|\bar{s}\rangle|^2 n(\epsilon+E_{s'}-E_{\bar{s}})\\ & \times F(\epsilon,\epsilon+E_{s'}-E_{\bar{s}})]+\pi\lambda^2(\langle s|\hat{S}|s\rangle\\ & -\langle s'|\hat{S}|s'\rangle)^2 n(\epsilon)F(\epsilon,\epsilon)+O(\lambda^3),\end{aligned} \tag{41}$$

in agreement with the results of Ref. [5]. We notice that the complete equations for the off-diagonal matrix elements couple in general different energies because of the integrals over the environment energy ϵ'.

The evolution equations for the populations of the states $|s\rangle$ of the system can be obtained by neglecting the contributions from the quantum coherences, i.e., by neglecting the terms involving off-diagonal elements of $P_{ss'}(\epsilon;t)$. This is justified in the weak-coupling limit as long as the coherences vanish or are negligible in the initial conditions, i.e., $P_{ss'}(\epsilon;0)=0$ for $s\neq s'$. Accordingly, we obtain the following evolution equations for the populations:

$$\begin{aligned}\dot{P}_{ss}(\epsilon;t)\simeq 2\pi\lambda^2\sum_{s'}|\langle s|\hat{S}|s'\rangle|^2 F(\epsilon,\epsilon+E_s-E_{s'})\\ \times[n(\epsilon)P_{s's'}(\epsilon+E_s-E_{s'};t)\\ -n(\epsilon+E_s-E_{s'})P_{ss}(\epsilon;t)].\end{aligned} \tag{42}$$

This equation is a kind of Pauli equation established with the Fermi golden rule and the conversation of energy in the transitions. Indeed, if a transition happens from a state in which the energy of the system is E_s and the one of the environment ϵ to a state in which the system has energy $E_{s'}$, the final energy of the environment should be $\epsilon'=\epsilon+E_s-E_{s'}$, which is well expressed by Eq. (42). Nevertheless, Eq. (42) rules the populations of the states s of the system with the extra information given by the distribution over the environment energy ϵ, which is not a feature of the standard Pauli equation and which turns out to be of importance to understand the relaxation inside a nanoscopic isolated system.

Our Markovian master equation (38) is more general than an equation for the populations because it also describes the time evolution of the distributions of the quantum coherences over the energy of the environment, as shown in the following sections.

B. Comparison with the Redfield master equation

We now discuss the conceptual differences between our quantum master equation and another one known as the Redfield master equation. This equation is well known in the context of nuclear magnetic resonance (NMR) where it describes the time evolution of nuclear spins interacting with their environment.

The Redfield master equation describes the time evolution of the system density matrix obtained tracing out from the total density matrix the degrees of freedom of the environment

$$\hat{\rho}_S(t)=\mathrm{Tr}_B\hat{\rho}(t). \tag{43}$$

The Redfield equation is derived by using the closure approximation that the total density matrix keeps the form

$$\hat{\rho}(t)=\hat{\rho}_S(t)\otimes\hat{\rho}_B \tag{44}$$

during the whole time evolution, where $\hat{\rho}_B$ does not depend on time. The Redfield master equation is derived in the weak-coupling limit by a method similar to the one of the previous section to get

$$\begin{aligned}\dot{\hat{\rho}}_S(t)=&-i[\hat{H}_S,\hat{\rho}_S(t)]-\lambda^2\hat{S}\int_0^t d\tau\,\alpha(\tau)\hat{S}(-\tau)\hat{\rho}_S(t)\\ &+\lambda^2\hat{S}\hat{\rho}_S(t)\int_0^t d\tau\alpha^*(\tau)\hat{S}(-\tau)\\ &+\lambda^2\int_0^t d\tau\,\alpha(\tau)\hat{S}(-\tau)\hat{\rho}_S(t)\hat{S}\\ &-\lambda^2\hat{\rho}_S(t)\int_0^t d\tau\,\alpha^*(\tau)\hat{S}(-\tau)\hat{S}+O(\lambda^3),\end{aligned} \tag{45}$$

with the correlation function of the environment operators

$$\alpha(t)=\langle\hat{B}(t)\hat{B}(0)\rangle=\mathrm{Tr}_B\hat{\rho}_B\hat{B}(t)\hat{B}(0). \tag{46}$$

Equation (45) is a *non-Markovian Redfield equation*. The non-Markovianity comes from the fact that the integrals over expressions containing the correlation function depend on time. The density matrix of the system can be represented in the basis of the system eigenstates as

$$\eta_{ss'}(t)\equiv\langle s|\hat{\rho}_S(t)|s'\rangle. \tag{47}$$

In this representation, the non-Markovian Redfield equation has the following form:

$$\begin{aligned}\dot{\eta}_{ss'}(t)=&-i(E_s-E_{s'})\eta_{ss'}(t)\\ &-\lambda^2\sum_{\overline{s},\overline{s}'}\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\int_0^t d\tau\{\langle s|\hat{S}|\overline{s}'\rangle\\ &\times\langle\overline{s}'|\hat{S}|\overline{s}\rangle\,\eta_{\overline{s}s'}(t)e^{+i(\epsilon-\epsilon'+E_{\overline{s}}-E_{\overline{s}'})\tau}-\langle s|\hat{S}|\overline{s}\rangle\\ &\times\langle\overline{s}'|\hat{S}|s'\rangle\,\eta_{\overline{s}\overline{s}'}(t)e^{+i(\epsilon-\epsilon'+E_{\overline{s}}-E_s)\tau}-\langle s|\hat{S}|\overline{s}\rangle\\ &\times\langle\overline{s}'|\hat{S}|s'\rangle\,\eta_{\overline{s}\overline{s}'}(t)e^{-i(\epsilon-\epsilon'+E_{\overline{s}'}-E_{s'})\tau}+\langle\overline{s}'|\hat{S}|\overline{s}\rangle\\ &\times\langle\overline{s}|\hat{S}|s'\rangle\,\eta_{s\overline{s}'}(t)e^{-i(\epsilon-\epsilon'+E_{\overline{s}'}-E_{\overline{s}})\tau}\}+O(\lambda^3).\end{aligned} \tag{48}$$

If the environment is large enough, the correlation function in Eq. (45) goes to zero after a certain time. This time, called the environment correlation time τ_{corr}, determines the time scale of the environment dynamics. If we perform the *Markovian approximation* that consists of putting the upper bound of the time integral in the non-Markovian Redfield equation to infinity, one gets the standard Redfield equation. We notice that, in doing so, the time evolution may be spoiled on a time scale of order τ_{corr} unless some use is made of some slipped initial conditions [11,12]. Performing this Markovian approximation, one gets the standard (Markovian) *Redfield equation* given by Eq. (45) with $\int_0^t$ replaced by $\int_0^\infty$. As shown in Refs. [11,12], the use of this Redfield Markovian equation needs to be supplemented by a slippage of initial conditions.

In order to compare the Redfield equation with our master equation derived in the previous section, we consider the case where the environment is initially in the *microcanonical* state:

$$\hat{\rho}_B = \frac{\delta(\epsilon - \hat{H}_B)}{\mathrm{Tr}_B \delta(\epsilon - \hat{H}_B)} = \frac{\delta(\epsilon - \hat{H}_B)}{n(\epsilon)}. \tag{49}$$

Having chosen the microcanonical density matrix (49) for the environment, the correlation function (46) takes the form

$$\begin{aligned}\alpha(\tau,\epsilon) &= \frac{1}{n(\epsilon)} \mathrm{Tr}_B \delta(\epsilon - \hat{H}_B) \hat{B}(\tau) \hat{B} \\ &= \frac{1}{n(\epsilon)} \int d\epsilon' \, \mathrm{Tr}_B \delta(\epsilon - \hat{H}_B) \hat{B}(\tau) \delta(\epsilon' - \hat{H}_B) \hat{B} \\ &= \int d\epsilon' n(\epsilon') F(\epsilon,\epsilon') e^{i(\epsilon - \epsilon')\tau}.\end{aligned} \tag{50}$$

In the basis of the system eigenstates, the Redfield equation takes the form

$$\begin{aligned}\dot{\eta}_{ss'}(t) = {}& -i(E_s - E_{s'})\eta_{ss'}(t) - i\lambda^2 \sum_{\overline{s},\overline{s}'} \Bigg\{ \Bigg[\int d\epsilon' n(\epsilon') F(\epsilon,\epsilon') \mathrm{P} \frac{1}{\epsilon - \epsilon' + E_{\overline{s}} - E_{\overline{s}'}} \Bigg] [\langle s|\hat{S}|\overline{s}'\rangle\langle\overline{s}'|\hat{S}|\overline{s}\rangle \eta_{\overline{s}s'}(t) - \langle\overline{s}|\hat{S}|\overline{s}'\rangle \\ & \times \langle\overline{s}'|\hat{S}|s'\rangle \eta_{s\overline{s}}(t)] + \int d\epsilon' n(\epsilon') F(\epsilon,\epsilon') \Bigg[\mathrm{P}\frac{1}{\epsilon - \epsilon' + E_{\overline{s}'} - E_{s'}} - \mathrm{P}\frac{1}{\epsilon - \epsilon' + E_{\overline{s}} - E_s} \Bigg] \langle s|\hat{S}|\overline{s}\rangle\langle\overline{s}'|\hat{S}|s'\rangle \eta_{\overline{s}\overline{s}'}(t) \Bigg\} \\ & - \pi\lambda^2 \sum_{\overline{s},\overline{s}'} \{ n(\epsilon + E_{\overline{s}} - E_{\overline{s}'}) F(\epsilon, \epsilon + E_{\overline{s}} - E_{\overline{s}'}) [\langle s|\hat{S}|\overline{s}'\rangle\langle\overline{s}'|\hat{S}|\overline{s}\rangle \eta_{\overline{s}s'}(t) + \langle\overline{s}|\hat{S}|\overline{s}'\rangle\langle\overline{s}'|\hat{S}|s'\rangle \eta_{s\overline{s}}(t)] \\ & - [n(\epsilon + E_{\overline{s}'} - E_{s'}) F(\epsilon, \epsilon + E_{\overline{s}'} - E_{s'}) + n(\epsilon + E_{\overline{s}} - E_s) F(\epsilon, \epsilon + E_{\overline{s}} - E_s)] \langle s|\hat{S}|\overline{s}\rangle\langle\overline{s}'|\hat{S}|s'\rangle \eta_{\overline{s}\overline{s}'}(t) \} + O(\lambda^3).\end{aligned} \tag{51}$$

The off-diagonal elements of the system density matrix individually obey the equations

$$\dot{\eta}_{ss'}(t) \simeq \{ -i[\tilde{E}_s(\epsilon) - \tilde{E}_{s'}(\epsilon)] - \Gamma_{ss'}(\epsilon) \} \eta_{ss'}(t), \tag{52}$$

with the same Lamb shifts (40) and damping rates (41) as in our master equation and as expected from Ref. [5]. There is no difference between our quantum master equation and the Redfield one at this stage.

On the other hand, the Redfield equation predicts an evolution of the populations ruled by the following equation obtained by neglecting all the contributions coming from the coherences in Eq. (51):

$$\begin{aligned}\dot{\eta}_{ss}(t) = {}& 2\pi\lambda^2 \sum_{s'} |\langle s|\hat{S}|s'\rangle|^2 [F(\epsilon, \epsilon + E_{s'} - E_s) \\ & \times n(\epsilon + E_{s'} - E_s) \eta_{s's'}(t) - F(\epsilon, \epsilon + E_s - E_{s'}) \\ & \times n(\epsilon + E_s - E_{s'}) \eta_{ss}(t)].\end{aligned} \tag{53}$$

This equation is the same as the master equation for the populations derived by Cohen-Tannoudji and co-workers in Ref. [5].

We notice that important differences now exists between the population equation (53) obtained from the Redfield equation and the other population equation (42) obtained from our master equation. Both equations describe the evolution of the populations as a random walk process in the spectrum. However, these processes are significantly different for Eqs. (42) and (53). Let us focus on the evolution of the probability to be on a system state corresponding to the system energy E_s. In both equations we see that for the loss contributions to the evolution coming from the jumps from an energy E_s to an energy $E_{s'}$, the density of states of the environment is modified by the energy $E_s - E_{s'}$. This is consistent with the Fermi golden rule applied to the total system and, thus, keeps the total energy constant. We care now on the gain contributions to the evolution. In our equation (42), we see that for these contributions due to jumps from the system energy $E_{s'}$ to E_s, the density of states of the environment is modified by the energy $E_{s'} - E_s$. This is also consistent with the Fermi golden rule applied to the total system and, thus, keeps the total energy constant. However, for the Redfield equation we see that for the jumps from an energy $E_{s'}$ to an energy E_s, the density of states of the environment is not modified by the energy $E_{s'} - E_s$, which is not consistent with the Fermi golden rule applied to the total system and does not keep the total energy constant.

One can represent, for the Markovian case, the transitions described by Eqs. (42) and (53) in a plane of the system energy versus the environment energy. In Figs. 1 and 2 we have depicted the energy exchanges described, respectively, by the Redfield equation and our equation in the Markovian limit for two different systems. Transitions between the system and the environment have to preserve the energy of the total system according to the Fermi golden rule and have therefore to occur along diagonal lines of the plane. One can see in Figs. 1 and 2 that only our equation satisfies this

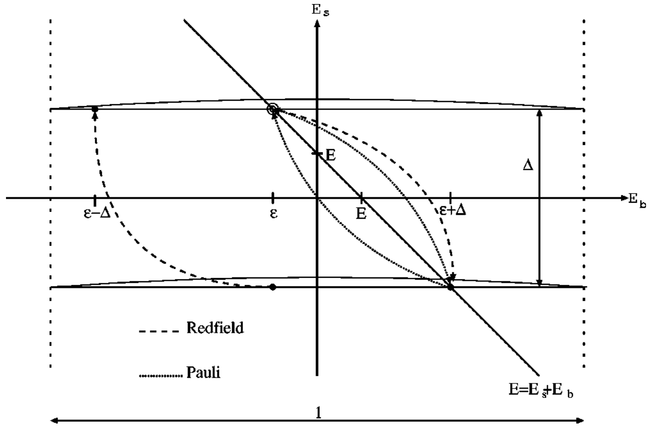

FIG. 1. Schematic representation of the energy exchanges described, respectively, by the Redfield and by our master equation in the Markovian limit for a two-level system model, in the plane of the system energy E_S versus the environment energy E_B. The energy splitting between the two levels of the system is denoted by Δ. The energy spectrum of the system is discrete (two levels) while the one of the environment is a quasicontinuum represented by the density of states given by the Wigner semicircular law (88) of width equal to unity. The total energy of the system is given by $E=E_S+E_B$, which corresponds to the diagonal line. The initial condition is denoted by two empty superposed circles. We see that transitions preserving the total energy have to occur along the diagonal line $E=E_S+E_B$. Doing this, they satisfy the Fermi golden rule for the total system. One can see that only our master equation satisfies this condition (dotted transition lines). The Redfield equation describes transitions that occur along a vertical line at constant environment energy and is therefore wrong (dashed transition lines).

condition. The Redfield equation describes transitions that occur along a vertical line at constant environment energy and is therefore not consistent with energy conservation in the total system. This is acceptable if the environment is sufficiently large and has an arbitrarily large energy. However, this is inadequate if the total energy of the system and the environment is finite as in nanoscopic systems, in which case our master should replace the Redfield equation.

We can summarize as follows the differences between our quantum master equation (38) and the Redfield equation (51). The derivation of both equations is based on the perturbative expansion of the total density matrix, but a specific form is imposed in each equation to the total density matrix [see Eqs. (10) and (44)]. The consequence of this choice can be seen on the reduced density matrix of the system. In the Redfield theory, we have

$$\hat{\rho}_S(t)=\sum_{s,s'} |s\rangle\, \eta_{ss'}(t)\langle s'|, \tag{54}$$

while, for our master equation, using Eq. (12) we have

$$\hat{\rho}_S(t)=\sum_{s,s'} \int d\epsilon |s\rangle P_{ss'}(\epsilon;t)\langle s'|. \tag{55}$$

The system density matrix is related to the distribution functions according to

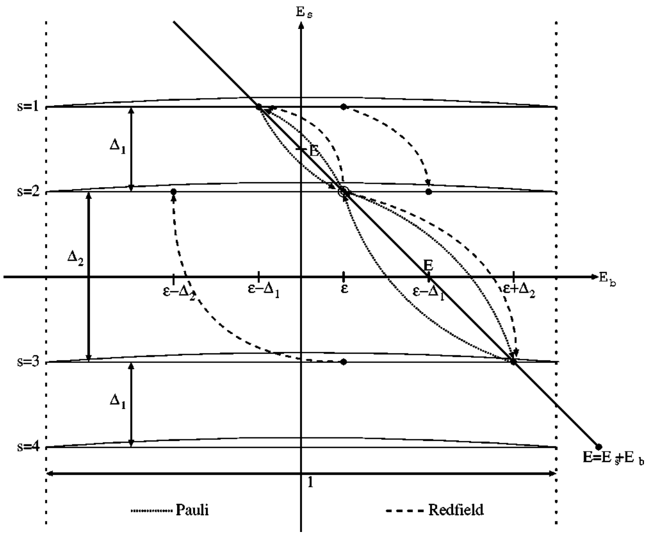

FIG. 2. Generalization of the previous Fig. 1 for the case where the system has more than two levels (here four levels). One can see that the system levels (horizontal lines) that do not intersect the total energy diagonal line $E=E_S+E_B$ within the environment energy spectrum delimited by the sparse-dotted vertical lines do not participate in the dynamics.

$$\langle s|\hat{\rho}_S(t)|s'\rangle = \eta_{ss'}(t)=\int d\epsilon\, P_{ss'}(\epsilon;t). \tag{56}$$

We see that, in our master equation, the matrix elements of the system density matrix are decomposed on the energy of the environment. This is not the case for the Redfield equation. The decomposition allows us to correlate the states of the system with the states of the environment. This is the main point of our master equation. The density matrix adopted for the Redfield equation cannot describe such correlations. In the Redfield equation, during the evolution, the environment is always in the same state while, in our master equation, the state of the environment is determined by the state of the system. As a consequence, we obtain a description which is consistent with energy conservation thanks to our master equation.

III. APPLICATION TO THE SPIN-ENVIRONMENT MODEL

In this section we consider a specific class of two-level systems interacting with an environment. The two-level system may be supposed to be a spin. An example is the spin-boson model in which the environment is a set of harmonic oscillators behaving as phonons [19].

The Hamiltonian of the spin-environment model we consider here is the following:

$$\hat{H}_{\rm tot}=\frac{\Delta}{2}\hat{\sigma}_z+\hat{H}_B+\lambda\,\hat{\sigma}_x\hat{B}. \tag{57}$$

The eigenvalue equation of the system is

$$\hat{H}_S|s\rangle = \frac{\Delta}{2}\hat{\sigma}_z|s\rangle = s\,\frac{\Delta}{2}|s\rangle, \tag{58}$$

where $s=\pm 1$. Like in Sec. II, we first derive our master equation and then the Redfield equation in order to compare both equations.

A. Using our master equation

Let us now apply our master equation to the spin-environment model. In our theory and for a two-level system, the total density matrix becomes

$$\hat{\rho}(t) = \frac{1}{n(\hat{H}_B)}[P_{++}(\hat{H}_B;t)|+\rangle\langle+| + P_{+-}(\hat{H}_B;t)|+\rangle\langle-| + P_{-+}(\hat{H}_B;t)|-\rangle\langle+| + P_{--}(\hat{H}_B;t)|-\rangle\langle-|]. \tag{59}$$

For the spin-environment model, our non-Markovian master equation (36) is given by

$$\begin{aligned}\dot{P}_{++}(\epsilon;t) = {}& -\lambda^2 P_{++}(\epsilon;t)\int d\epsilon' F(\epsilon,\epsilon')n(\epsilon')\\ &\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}]\\ &+\lambda^2 n(\epsilon)\int d\epsilon' F(\epsilon,\epsilon')P_{--}(\epsilon';t)\\ &\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}],\end{aligned} \tag{60}$$

$$\begin{aligned}\dot{P}_{--}(\epsilon;t) = {}& -\lambda^2 P_{--}(\epsilon;t)\int d\epsilon' F(\epsilon,\epsilon')n(\epsilon')\\ &\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}]\\ &+\lambda^2 n(\epsilon)\int d\epsilon' F(\epsilon,\epsilon')P_{++}(\epsilon';t)\\ &\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}],\end{aligned} \tag{61}$$

$$\begin{aligned}\dot{P}_{+-}(\epsilon;t) = {}& -i\Delta P_{+-}(\epsilon;t)-\lambda^2 P_{+-}(\epsilon;t)\\ &\times\int d\epsilon' F(\epsilon,\epsilon')n(\epsilon')\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}\\ &+e^{-i(\epsilon-\epsilon'-\Delta)\tau}]+\lambda^2 n(\epsilon)\\ &\times\int d\epsilon' F(\epsilon,\epsilon')P_{-+}(\epsilon';t)\\ &\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}],\end{aligned} \tag{62}$$

and a further equation for $\dot{P}_{-+}(\epsilon;t)$ given by the complex conjugate of Eq. (62).

We observe that the diagonal and off-diagonal elements of $P_{ss'}(\epsilon;t)$ obey decoupled equations in the case of the spin-environment model. Therefore, the time evolution of the populations is independent of the time evolution of the quantum coherences. We now perform the *Markovian approximation* that consists of putting the upper bound of the time integral to infinity. Using Eq. (37), we find

$$\begin{aligned}\dot{P}_{++}(\epsilon;t) = {}& 2\pi\lambda^2 F(\epsilon,\epsilon+\Delta)[n(\epsilon)P_{--}(\epsilon+\Delta;t)\\ &-n(\epsilon+\Delta)P_{++}(\epsilon;t)],\end{aligned} \tag{63}$$

$$\begin{aligned}\dot{P}_{--}(\epsilon;t) = {}& 2\pi\lambda^2 F(\epsilon,\epsilon-\Delta)[n(\epsilon)P_{++}(\epsilon-\Delta;t)\\ &-n(\epsilon-\Delta)P_{--}(\epsilon;t)],\end{aligned} \tag{64}$$

$$\begin{aligned}\dot{P}_{+-}(\epsilon;t) = {}& -i\Delta P_{+-}(\epsilon;t)+i\lambda^2\int d\epsilon' F(\epsilon,\epsilon')\\ &\times \mathcal{P}\frac{2\Delta}{(\epsilon-\epsilon')^2-\Delta^2}[n(\epsilon')P_{+-}(\epsilon;t)\\ &+n(\epsilon)P_{-+}(\epsilon';t)]-\pi\lambda^2[n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)\\ &+n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)]P_{+-}(\epsilon;t)+\pi\lambda^2 n(\epsilon)\\ &\times[F(\epsilon,\epsilon+\Delta)P_{-+}(\epsilon+\Delta;t)\\ &+F(\epsilon,\epsilon-\Delta)P_{-+}(\epsilon-\Delta;t)].\end{aligned} \tag{65}$$

We notice that during the time evolution of the populations, the following quantity remains a constant of motion:

$$P(\epsilon;t)\equiv P_{++}(\epsilon;t)+P_{--}(\epsilon+\Delta;t)=P(\epsilon;0). \tag{66}$$

Accordingly, the difference of the populations defined as

$$Z(\epsilon;t)\equiv P_{++}(\epsilon;t)-P_{--}(\epsilon+\Delta;t) \tag{67}$$

obeys the differential equation

$$\begin{aligned}\dot{Z}(\epsilon;t) = {}& 2\pi\lambda^2[n(\epsilon)-n(\epsilon+\Delta)]F(\epsilon,\epsilon+\Delta)\mathrm{P}(\epsilon;0)\\ &-2\pi\lambda^2[n(\epsilon)+n(\epsilon+\Delta)]F(\epsilon,\epsilon+\Delta)Z(\epsilon;t),\end{aligned} \tag{68}$$

the solution of which is given by

$$Z(\epsilon;t)=Z(\epsilon;\infty)+[Z(\epsilon;0)-Z(\epsilon;\infty)]e^{-\gamma_{\mathrm{Pauli}}t} \tag{69}$$

with the asymptotic equilibrium value

$$Z(\epsilon;\infty)=\frac{n(\epsilon)-n(\epsilon+\Delta)}{n(\epsilon)+n(\epsilon+\Delta)}\mathrm{P}(\epsilon;0) \tag{70}$$

and the relaxation rate

$$\gamma_{\mathrm{Pauli}}=2\pi\lambda^2[n(\epsilon)+n(\epsilon+\Delta)]F(\epsilon,\epsilon+\Delta). \tag{71}$$

Therefore, the populations relax to their asymptotic equilibrium values for each pair of energies ϵ and $\epsilon+\Delta$ of the environment, keeping constant the initial distribution of the quantity $P(\epsilon;0)$.

The time evolution of the distribution functions $P_{\pm\mp}(\epsilon;t)$ of the quantum coherences is more complicated because there is now a coupling between a continuum of values of the environment energy instead of only two values. Accordingly, the distributions of quantum coherence is ruled by a couple of two integro-differential equations, instead of an ordinary differential equation.

B. Using the Redfield equation

For the spin-environment model, the non-Markovian and Markovian Redfield equations can be derived from Eqs. (48) and (51). Using Eq. (48), the non-Markovian Redfield equations here write

$$\begin{aligned}\dot{\eta}_{++}(t)=&-\lambda^2\eta_{++}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}]\\&+\lambda^2\eta_{--}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}],\end{aligned}\tag{72}$$

$$\begin{aligned}\dot{\eta}_{--}(t)=&-\lambda^2\eta_{--}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}]\\&+\lambda^2\eta_{++}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}],\end{aligned}\tag{73}$$

$$\begin{aligned}\dot{\eta}_{+-}(t)=&-i\Delta\eta_{+-}(t)-\lambda^2\eta_{+-}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}]\\&+\lambda^2\eta_{-+}(t)\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\int_0^t d\tau[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}],\end{aligned}\tag{74}$$

and a further equation for $\eta_{-+}(t)$ given by the complex conjugate of Eq. (74).

Here again, there is a decoupling between the time evolutions of the populations and of the quantum coherences.

Taking the Markovian approximation by replacing $\int_0^t$ into $\int_0^\infty$ and using Eq. (37), we get the Markovian Redfield equations for the spin-environment model:

$$\begin{aligned}\dot{\eta}_{++}(t)=&2\pi\lambda^2[n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)\eta_{--}(t)\\&-n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)\eta_{++}(t)],\end{aligned}\tag{75}$$

$$\begin{aligned}\dot{\eta}_{--}(t)=&2\pi\lambda^2[n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)\eta_{++}(t)\\&-n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)\eta_{--}(t)],\end{aligned}\tag{76}$$

$$\begin{aligned}\dot{\eta}_{+-}(t)=&-i\Delta\eta_{+-}(t)+i\lambda^2\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')\\&\times\mathrm{P}\frac{2\Delta}{(\epsilon-\epsilon')^2-\Delta^2}[\eta_{+-}(t)+\eta_{-+}(t)]-\pi\lambda^2\\&\times[n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)+n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)]\\&\times[\eta_{+-}(t)-\eta_{-+}(t)].\end{aligned}\tag{77}$$

The populations of the two-level system are controlled by the z component of the spin defined as the difference

$$z_{\text{Redfield}}(t)=\eta_{++}(t)-\eta_{--}(t).\tag{78}$$

According to the Markovian Redfield equations (75) and (76), the z component obeys the differential equation

$$\begin{aligned}\dot{z}_{\text{Redfield}}=&2\pi\lambda^2[n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)-n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)]\\&-2\pi\lambda^2[n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)\\&+n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)]z_{\text{Redfield}}.\end{aligned}\tag{79}$$

Its solution is given by

$$\begin{aligned}z_{\text{Redfield}}(t)=&z_{\text{Redfield}}(\infty)\\&+[z_{\text{Redfield}}(0)-z_{\text{Redfield}}(\infty)]e^{-\gamma_{\text{Redfield}}t},\end{aligned}\tag{80}$$

with the equilibrium value

$$z_{\text{Redfield}}(\infty)=\frac{n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)-n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)}{n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)+n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)},\tag{81}$$

and the relaxation rate

$$\begin{aligned}\gamma_{\text{Redfield}}=&2\pi\lambda^2[n(\epsilon-\Delta)F(\epsilon,\epsilon-\Delta)\\&+n(\epsilon+\Delta)F(\epsilon,\epsilon+\Delta)].\end{aligned}\tag{82}$$

We notice that the rate predicted by the Redfield equation coincides with the one predicted by our master equation only in the limit $\Delta = 0$. A more important difference appears in the asymptotic equilibrium values for the z component of the spin predicted by both equations. These differences find their origin in the problem of conservation of energy with the Redfield equation, as explained above. Comparison with numerical data will confirm this explanation in a following section in the case of the spin-GORM model.

IV. APPLICATION TO THE SPIN-GORM MODEL

In order to confront our master equation and the Redfield equation with numerical data and test their respective domains of validity, we now apply our theory to a specific class of two-level systems interacting with an environment, for which the environment operators are Gaussian orthogonal random matrices (GORM). We call this model the spin-GORM model and its detailed properties will be described elsewhere [20].

The system is a two-level system, while the environment is supposed to be a system with a very complex dynamics. Here, the term complex is used in a generic way. The complexity can come, for example, from the fact that the corresponding classical system is chaoticlike in a quantum billiard or for the hydrogen atom in a strong magnetic field [21,22]. It can also come from a large number of coupling between states in an interacting many-body system like those appearing in nuclear physics [22] or in systems of interacting fermions like quantum computers [22]. A well-known method, developed by Wigner in the 1950s, for modeling the energy spectrum of a complex quantum system containing many states interacting with each other, consists of assuming that their Hamiltonian is a random matrix [23–25]. Here, we suppose that the Hamiltonian of the environment is a Gaussian orthogonal random matrix (GORM). The interaction between the spin and the environment is given by a coupling operator which is the product of a system and environment operators. The latter is also represented by a GORM because of its complex interaction with the many degrees of freedom of the environment. Such random-matrix models have recently turned out to be of great relevance for the discussion of relaxation and dissipation in quantum systems [16,26–29].

The spin-GORM model can therefore be considered as a particular case of the spin-environment model in which the environment operators are GORM. The Hamiltonian of the spin-GORM model is thus given by

$$\hat{H}_{\text{tot}} = \frac{\Delta}{2}\hat{\sigma}_z + \hat{H}_B + \lambda\,\hat{\sigma}_x \hat{B} \tag{83}$$

where the Hamiltonian of the environment is

$$\hat{H}_B = \frac{1}{\sqrt{8N}}\hat{X}, \tag{84}$$

and the environment coupling operator by

$$\hat{B} = \frac{1}{\sqrt{8N}}\hat{X}'. \tag{85}$$

$\hat{X}$ and $\hat{X}'$ are two statistically independent $N/2 \times N/2$ random matrices belonging to the Gaussian orthogonal ensemble (GOE) of probability density

$$p(\hat{X}) = \mathcal{C} \exp(-a_{\hat{X}}\,\mathrm{Tr}\,\hat{X}^2), \tag{86}$$

with $a_{\hat{X}} = \frac{1}{2}$ and a normalization constant $\mathcal{C}$. $N/2$ is the number of states of the environment. The off-diagonal and diagonal elements of $\hat{X}$ are independent Gaussian random numbers with mean zero and standard deviations $\sigma_{\text{off-diag.}} = 1$ and $\sigma_{\text{diag}} = \sqrt{2}$, respectively.

In the limit $N \rightarrow \infty$, the density of states of the environment gets smooth and can be calculated by an average over the random-matrix ensemble

$$n(\epsilon) = \overline{\sum_{b=1}^{N/2} \delta(\epsilon - E_b)}. \tag{87}$$

It is known that the GOE level density is given by the Wigner semicircular law

$$n(\epsilon) = \begin{cases} \dfrac{4N}{\pi}\sqrt{\frac{1}{4} - \epsilon^2} & \text{if } |\epsilon| < \frac{1}{2} \\ 0 & \text{if } |\epsilon| \geq \frac{1}{2}\,. \end{cases} \tag{88}$$

The random matrices are normalized so that the level density of the environment has a width equal to unity. To simplify the notations in the following, we use the convention

$$\sqrt{x} \equiv \begin{cases} \sqrt{x} & \text{if } 0 < x \\ 0 & \text{if } x \leq 0. \end{cases} \tag{89}$$

For the following, we also need to evaluate the function $F(\epsilon, \epsilon')$ for our random-matrix model. For this purpose, we need the random-matrix average of the quantity (28). Since, in the GOE, we have that

$$\overline{|\langle b|\hat{B}|b\rangle|^2} = \frac{1}{4N}, \tag{90}$$

$$\overline{|\langle b|\hat{B}|b'\rangle|^2} = \frac{1}{8N}, \tag{91}$$

we find that

$$
\begin{aligned}
\overline{\mathrm{Tr}_B \delta(\epsilon-\hat{H}_B)\hat{B}\,\delta(\epsilon'-\hat{H}_B)\hat{B}} &= \overline{\sum_{b,b'} \delta(\epsilon-E_b)\,\delta(\epsilon'-E_{b'})|\langle b|\hat{B}|b'\rangle|^2} \\
&= \sum_b \overline{\delta(\epsilon-E_b)\,\delta(\epsilon'-E_b)}\;\overline{|\langle b|\hat{B}|b\rangle|^2} + \sum_{b\neq b'} \overline{\delta(\epsilon-E_b)\,\delta(\epsilon'-E_{b'})}\;\overline{|\langle b|\hat{B}|b'\rangle|^2} \\
&= \frac{1}{4N}\overline{\sum_b \delta(\epsilon-E_b)\,\delta(\epsilon'-E_b)} + \frac{1}{8N}\overline{\sum_{b\neq b'} \delta(\epsilon-E_b)\,\delta(\epsilon'-E_{b'})} \\
&= \frac{1}{8N}\overline{\sum_b \delta(\epsilon-E_b)\,\delta(\epsilon'-E_b)} + \frac{1}{8N}\overline{\sum_{b,b'} \delta(\epsilon-E_b)\,\delta(\epsilon'-E_{b'})} \\
&\simeq \frac{1}{8N}\delta(\epsilon-\epsilon')n(\epsilon) + \frac{1}{8N}n(\epsilon)n(\epsilon'). \qquad (92)
\end{aligned}
$$

In the limit $N\to\infty$, the first term becomes negligible in front of the second term so that the comparison with Eq. (28) shows that for the spin-GORM model,

$$
F(\epsilon,\epsilon') \simeq \frac{1}{8N}. \qquad (93)
$$

The total system contains N states. The unperturbed density of states of the total system is schematically depicted in Fig. 3, for $\lambda=0$. The model has different regimes whether the splitting Δ between the two levels of the spin is larger or smaller than the width of the environment level density. The spin-GORM model can describe a large variety of physical situations. In the present paper we focus on the perturbative regimes ($\lambda \ll \hat{H}_B$). When Δ is larger than the width of the semicircular density of states of the environment, we are in a highly non-Markovian regime. The dynamics of the system is faster than that of the environment. On the other hand, when Δ is smaller than unity, we are in a Markovian regime because the dynamics of the environment is much faster then the one of the system.

Now, we apply our master equation and the Redfield equation to the spin-GORM model in both their Markovian and non-Markovian versions.

A. Using our master equation

We now apply our master equation (36) to the spin-GORM model. Using Eqs. (60)–(62), (88), and (93), we get the non-Markovian equations

$$
\begin{aligned}
\dot{P}_{++}(\epsilon;t) = &-\frac{\lambda^2}{\pi}P_{++}(\epsilon;t)\int d\epsilon' \sqrt{\frac{1}{4}-\epsilon'^2} \\
&\times \frac{\sin(\epsilon-\epsilon'+\Delta)t}{(\epsilon-\epsilon'+\Delta)} + \frac{\lambda^2}{\pi}\sqrt{\frac{1}{4}-\epsilon^2} \\
&\times \int d\epsilon' P_{--}(\epsilon';t)\frac{\sin(\epsilon-\epsilon'+\Delta)t}{(\epsilon-\epsilon'+\Delta)}, \qquad (94)
\end{aligned}
$$

$$
\begin{aligned}
\dot{P}_{--}(\epsilon;t) = &-\frac{\lambda^2}{\pi}P_{--}(\epsilon;t)\int d\epsilon' \sqrt{\frac{1}{4}-\epsilon'^2} \\
&\times \frac{\sin(\epsilon-\epsilon'-\Delta)t}{(\epsilon-\epsilon'-\Delta)} + \frac{\lambda^2}{\pi}\sqrt{\frac{1}{4}-\epsilon^2} \\
&\times \int d\epsilon' P_{++}(\epsilon';t)\frac{\sin(\epsilon-\epsilon'-\Delta)t}{(\epsilon-\epsilon'-\Delta)}, \qquad (95)
\end{aligned}
$$

$$
\begin{aligned}
\dot{P}_{+-}(\epsilon;t) = &-i\Delta P_{+-}(\epsilon;t) - \frac{\lambda^2}{2\pi}P_{+-}(\epsilon;t)\int d\epsilon' \\
&\times \sqrt{\frac{1}{4}-\epsilon'^2}\int_0^t d\tau\big[e^{i(\epsilon-\epsilon'+\Delta)\tau}+e^{-i(\epsilon-\epsilon'-\Delta)\tau}\big] \\
&+ \frac{\lambda^2}{2\pi}\sqrt{\frac{1}{4}-\epsilon^2}\int d\epsilon' P_{-+}(\epsilon';t) \\
&\times \int_0^t d\tau\big[e^{i(\epsilon-\epsilon'-\Delta)\tau}+e^{-i(\epsilon-\epsilon'+\Delta)\tau}\big]. \qquad (96)
\end{aligned}
$$

We notice that the equations for the populations are decoupled from the ones for the quantum coherences.

Performing the *Markovian approximation* and using $\lim_{t\to\infty}(\sin \omega t/\omega)=\pi\delta(\omega)$ and Eq. (37), we get

$$
\begin{aligned}
\dot{P}_{++}(\epsilon;t) = &-\lambda^2\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}P_{++}(\epsilon;t) \\
&+\lambda^2\sqrt{\frac{1}{4}-\epsilon^2}P_{--}(\epsilon+\Delta;t), \qquad (97)
\end{aligned}
$$

$$
\begin{aligned}
\dot{P}_{--}(\epsilon;t) = &-\lambda^2\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}P_{--}(\epsilon;t) \\
&+\lambda^2\sqrt{\frac{1}{4}-\epsilon^2}P_{++}(\epsilon-\Delta;t), \qquad (98)
\end{aligned}
$$

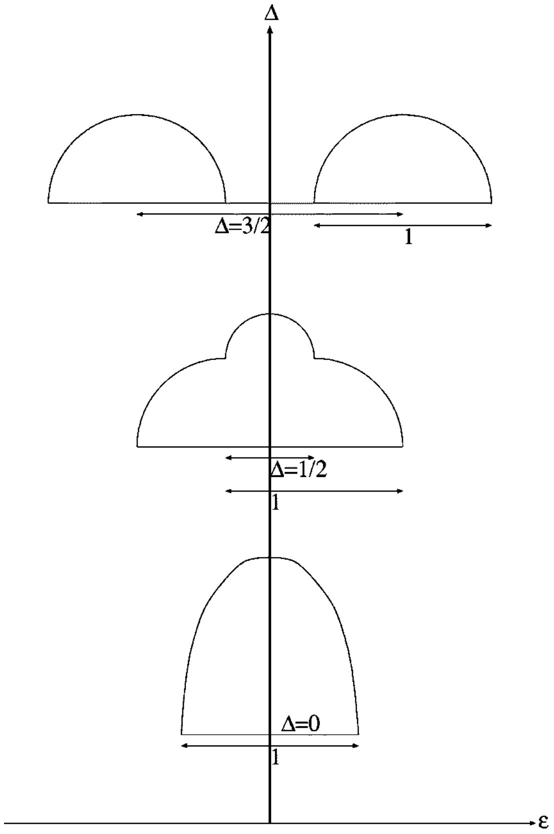

FIG. 3. Schematic representation of the smooth density of states (DOS) of the unperturbed spin-GORM model ($\lambda=0$) for different values of the energy splitting Δ of the spin. The horizontal axis is the environment energy ϵ while the vertical axis is the energy splitting Δ. In the lower and central parts, the splitting Δ is smaller than the width of the environment DOS. In the upper part, the splitting Δ is larger than the width of the DOS.

$$\dot{P}_{+-}(\epsilon;t)=-i\Delta P_{+-}(\epsilon;t)+i\frac{\lambda^2}{\pi}\int d\epsilon'\,\mathrm{P}\frac{\Delta}{(\epsilon-\epsilon')^2-\Delta^2}\times\left[\sqrt{\frac{1}{4}-\epsilon'^2}P_{+-}(\epsilon;t)+\sqrt{\frac{1}{4}-\epsilon^2}P_{-+}(\epsilon';t)\right]-\frac{\lambda^2}{2}\left[\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}+\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}\right]\times P_{+-}(\epsilon;t)+\frac{\lambda^2}{2}\sqrt{\frac{1}{4}-\epsilon^2}[P_{-+}(\epsilon+\Delta;t)+P_{-+}(\epsilon-\Delta;t)], \tag{99}$$

where the expressions and integrals over energy extend over the interval of definition of the level density $n(E)$ and of the distributions $P_{ss'}(E;t)$ which is always $-1/2<E<+1/2$, E being the argument of these functions.

We now focus our attention on the evolution of the populations. We see from Eqs. (97) and (98) that the transitions conserve the total energy of the system and environment so that the transitions occur between the only two energies ϵ and $\epsilon+\Delta$ of the environment. As a consequence, the quantity

$$P(\epsilon;t)\equiv P_{++}(\epsilon;t)+P_{--}(\epsilon+\Delta;t)=P(\epsilon;0) \tag{100}$$

is a constant of the motion for each energy ϵ of the environment, as already noticed with Eq. (66). The difference (67) of populations obeys the differential equation (68). If the initial distributions $P(\epsilon';0)$ and $Z(\epsilon';0)$ are Dirac delta distributions centered on the initial energy ϵ:

$$P(\epsilon';0)=\delta(\epsilon'-\epsilon), \tag{101}$$

$$Z(\epsilon';0)=\delta(\epsilon'-\epsilon)z_{\mathrm{Pauli}}(0). \tag{102}$$

The z component of the spin defined as

$$z_{\mathrm{Pauli}}(t)=\int d\epsilon\, Z(\epsilon;t) \tag{103}$$

obeys the same differential equation as the distribution $Z(\epsilon;t)$,

$$\dot{z}_{\mathrm{Pauli}}(t)=\lambda^2\left[\sqrt{\frac{1}{4}-\epsilon^2}-\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\right]-\lambda^2\left[\sqrt{\frac{1}{4}-\epsilon^2}+\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\right]z_{\mathrm{Pauli}}(t). \tag{104}$$

The solution of Eq. (104) is given by

$$z_{\mathrm{Pauli}}(t)=z_{\mathrm{Pauli}}(\infty)+[z_{\mathrm{Pauli}}(0)-z_{\mathrm{Pauli}}(\infty)]e^{-\gamma_{\mathrm{Pauli}}t}, \tag{105}$$

with the asymptotic equilibrium value

$$z_{\mathrm{Pauli}}(\infty)=\frac{\sqrt{\frac{1}{4}-\epsilon^2}-\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}}{\sqrt{\frac{1}{4}-\epsilon^2}+\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}}, \tag{106}$$

and the relaxation rate

$$\gamma_{\mathrm{Pauli}}=\lambda^2\left[\sqrt{\frac{1}{4}-\epsilon^2}+\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\right]. \tag{107}$$

With the convention (89), the expressions are nonvanishing only over the interval of definition of their argument. Figure 4 helps us to represent the different values that take Eqs. (106) and (107) in the space of the environment energy ϵ and of the splitting energy Δ of the two-level system.

B. Using the Redfield equation

For the spin-GORM model, the correlation function (46) can be calculated by performing a GOE average. Using the

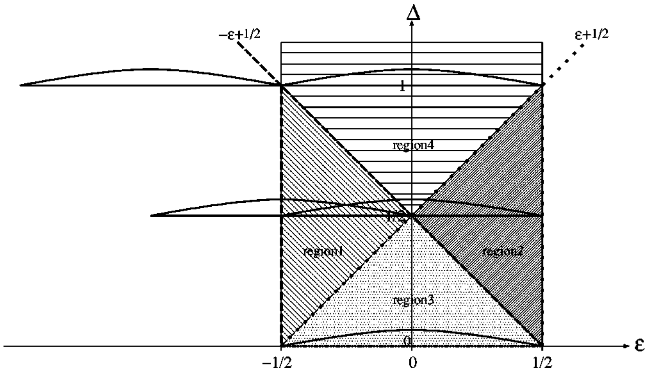

FIG. 4. Schematic representation of the different regimes of the spin-GORM model for situations where the initial state of the spin is $s=+1$, in the plane of the environment energy ϵ versus the spin energy splitting Δ. The different regions correspond to different values of the functions $n(\epsilon)$, $n(\epsilon+\Delta)$, and $n(\epsilon-\Delta)$, where $n(E)$ denotes the DOS defined by the semicircular law (88). One can take a value of the environment energy anywhere between $\epsilon=-\frac{1}{2}$ and $\epsilon=\frac{1}{2}$, where $n(\epsilon)\neq 0$. In region 1: $n(\epsilon+\Delta)\neq 0$ and $n(\epsilon-\Delta)=0$. In region 2: $n(\epsilon+\Delta)=0$ and $n(\epsilon-\Delta)\neq 0$. In region 3: $n(\epsilon+\Delta)\neq 0$ and $n(\epsilon-\Delta)\neq 0$. In region 4: $n(\epsilon+\Delta)=0$ and $n(\epsilon-\Delta)=0$. This figure is useful to evaluate equations such as Eqs. (106) and (107) and (115) and (116).

level density (88) and the value (93), the microcanonical correlation function (50) becomes

$$\begin{aligned}\alpha(\tau,\epsilon)&=\int d\epsilon' n(\epsilon')F(\epsilon,\epsilon')e^{i(\epsilon-\epsilon')\tau}\\&\simeq\int_{-1/2}^{+1/2}d\epsilon'\frac{4N}{\pi}\sqrt{\frac{1}{4}-\epsilon'^2}\,\frac{1}{8N}e^{i(\epsilon-\epsilon')\tau}\\&=\frac{J_1\left(\frac{\tau}{2}\right)}{4\tau}e^{i\epsilon\tau},\end{aligned}\tag{108}$$

in the limit $N\to\infty$, where $J_1(t)$ is the Bessel function of the first kind.

Therefore, using the Redfield equation (72)–(74) and the microcanonical correlation function of the spin-GORM model, we get

$$\begin{aligned}\dot{\eta}_{++}(t)=&-\lambda^2\eta_{++}(t)\int_0^t d\tau\cos[(\epsilon+\Delta)\tau]\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau}\\&+\lambda^2\eta_{--}(t)\int_0^t d\tau\cos[(\epsilon-\Delta)\tau]\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau},\end{aligned}\tag{109}$$

$$\begin{aligned}\dot{\eta}_{--}(t)=&-\lambda^2\eta_{--}(t)\int_0^t d\tau\cos[(\epsilon-\Delta)\tau]\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau}\\&+\lambda^2\eta_{++}(t)\int_0^t d\tau\cos[(\epsilon+\Delta)\tau]\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau},\end{aligned}\tag{110}$$

$$\begin{aligned}\dot{\eta}_{+-}(t)=&-i\Delta\eta_{+-}(t)-\lambda^2\eta_{+-}(t)\int_0^t d\tau e^{i\Delta\tau}\cos(\epsilon\tau)\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau}\\&+\lambda^2\eta_{-+}(t)\int_0^t d\tau e^{-i\Delta\tau}\cos(\epsilon\tau)\frac{J_1\left(\frac{\tau}{2}\right)}{2\tau}.\end{aligned}\tag{111}$$

These are the non-Markovian Redfield equations for the spin-GORM model. The Markovian Redfield equations for the spin-GORM model take the following forms:

$$\begin{aligned}\dot{\eta}_{++}(t)=&-\lambda^2\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\,\eta_{++}(t)\\&+\lambda^2\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}\,\eta_{--}(t),\end{aligned}\tag{112}$$

$$\begin{aligned}\dot{\eta}_{--}(t)=&-\lambda^2\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}\,\eta_{--}(t)\\&+\lambda^2\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\,\eta_{++}(t),\end{aligned}\tag{113}$$

$$\begin{aligned}\dot{\eta}_{+-}(t)=&-i\Delta\eta_{+-}(t)+i\frac{\lambda^2}{\pi}\int d\epsilon'\sqrt{\frac{1}{4}-\epsilon'^2}\\&\times\mathrm{P}\frac{\Delta}{(\epsilon-\epsilon')^2-\Delta^2}[\eta_{+-}(t)+\eta_{-+}(t)]\\&-\frac{\lambda^2}{2}\left[\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}+\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}\right]\\&\times[\eta_{+-}(t)-\eta_{-+}(t)].\end{aligned}\tag{114}$$

We focus on the evolution of the populations. The population of the two-level system is controlled by the z component of the spin by Eq. (78). According to the Markovian Redfield equations (112) and (113), the time evolution of the z component is given by Eq. (80) with the equilibrium value

$$z_{\mathrm{Redfield}}(\infty)=\frac{\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}-\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}}{\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}+\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}}, \tag{115}$$

and the relaxation rate

$$\gamma_{\mathrm{Redfield}}=\lambda^2\left[\sqrt{\frac{1}{4}-(\epsilon-\Delta)^2}+\sqrt{\frac{1}{4}-(\epsilon+\Delta)^2}\right]. \tag{116}$$

Figure 4 depicts the different regimes predicted by this equation in the space of the environment energy ϵ and the splitting energy Δ.

We observe that in the limit $\Delta\to 0$, where the energy scale of the system is much smaller than the one of the environment, both our master equation and the Redfield equation predict a similar value for the relaxation rate. However, differences appear for the value of the asymptotic value of the z component of the spin. As we explained here above, the reason is that our master equation is consistent with energy conservation in the total system albeit the Redfield equation is not. This problem spoils the applicability of the Redfield master equation if the environment is not arbitrarily large as we shall see in the next section.

V. NUMERICAL RESULTS AND DISCUSSION

The purpose of the present section is to compare the different master equations with exact numerical results obtained for the relaxation of the z component of the spin due to the interaction with its environment in the spin-GORM model. The initial condition of the spin is always the state $|+\rangle$. The environment is always taken in a microcanonical distribution at a given energy ϵ. The width of the energy shell of this microcanonical distribution is always equal to $\delta\epsilon=0.05$.

A general comment is here in order concerning the applicability of a master equation to a quantum system with a discrete energy spectrum. Indeed, beyond a time longer than the Heisenberg time (which is defined as the level density of the total system), quantum beats and recurrences appear due to the discreteness of the energy spectrum. Only, the decay before the Heisenberg time can be compared with the prediction of a quantum master equation. It turns out that the further condition $N\lambda^2>1$ should also be satisfied, which requires that the coupling parameter should not be too small with respect to the mean level spacing which goes as $1/N$. If this condition is not satisfied ($N\lambda^2<1$) the time evolution of individual systems present large quantum oscillations which widely deviate from the prediction of the master equation. On the other hand, if $N\lambda^2>1$, the deviations with respect to the predictions of the master equation are smaller than the signal itself and tend to decrease as $N\to\infty$ [20]. In the limit $N\to\infty$, the decay curve which is the solution of the master equation is approximately followed by a majority of realizations of the process by individual systems. In the figures given here, these deviations are not seen because of an averaging of the signal over $\chi=10$ individual systems. Besides the condition $N\lambda^2>1$, the coupling parameter should also be small enough to justify the perturbative treatment, typically $\lambda<0.3$.

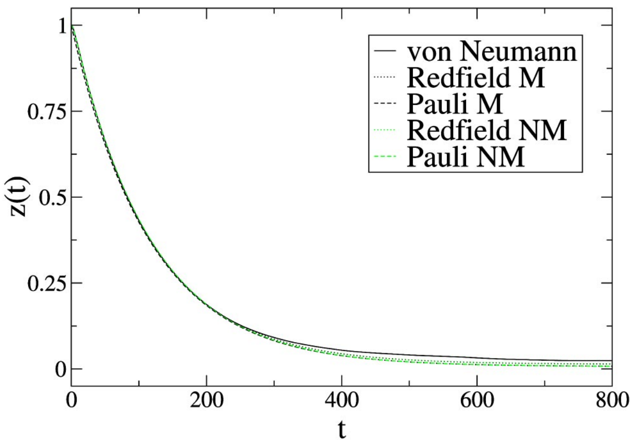

FIG. 5. Relaxation of the z component of the spin for the spin-GORM model for a very small spin energy splitting $\Delta=0.01$ with $\lambda=0.1$, $\epsilon=0.25$, $N=2000$, and $\chi=10$. The exact curve is given by integrating the von Neumann equation, which is compared with the solutions of the Pauli and Redfield Markovian (M) and non-Markovian (NM) equations. We see that all the perturbative equations give similar results in the present case.

The equations we are comparing are the following.

(i) The von Neumann equation describes the z component of the spin using Eq. (2) with the Hamiltonian (83). Averaging is carried out with χ realizations of the GORM Hamiltonian. This calculation does not involve any approximation and, therefore, gives the exact solution of the problem. All the following equations will be compared to this one.

(ii) The most general non-Markovian version of our master equation (36) using Eqs. (94) and (95), which we refer to as the Pauli non-Markovian (NM) equation.

(iii) The Markovian version (38) of our master equation, which we refer to as the Pauli Markovian (M) equation. For the spin-GORM model, this equation is given by Eqs. (97) and (98) and its solutions by Eqs. (105)–(107).

(iv) The Redfield non-Markovian equation (48) is given by Eqs. (109) and (110) for the spin-GORM model.

(v) The standard Redfield Markovian equation (51) is given by Eqs. (112) and (113) and its solutions by Eqs. (80) with Eqs. (115) and (116).

The results of the numerical calculation of the time evolution of the z component of the spin are depicted in Figs. 5–10 for different regimes of the spin-GORM model, i.e., for different values of the energy splitting Δ of the two-level system as well as of the environment energy ϵ. In all the cases, the coupling parameter is equal to $\lambda=0.1$.

Figures 5, 7, and 8 depict the global relaxation of the z component of the spin for increasing values of the energy splitting Δ. In accordance with what we argued before on theoretical grounds, we see in these figures that the larger the energy splitting Δ of the system is, the bigger is the difference between the Redfield and our master equation. We also

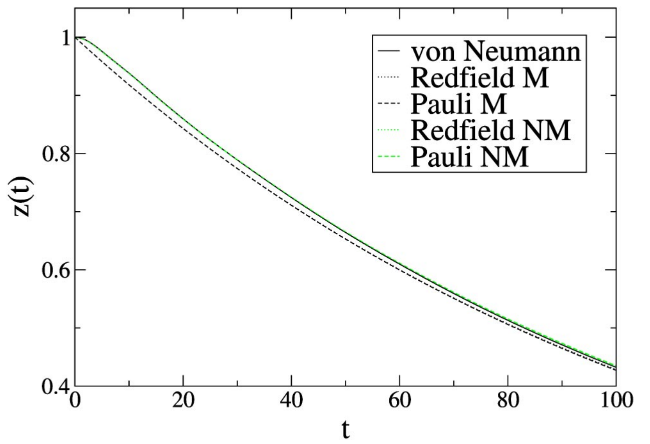

FIG. 6. Relaxation of the z component of the spin for the spin-GORM model in the same conditions $\Delta=0.01$, $\lambda=0.1$, $\epsilon=0.25$, $N=2000$, and $\chi=10$ as in Fig. 5 in order to show that, on a short time scale of the order of the correlation time of the environment $\tau_{\mathrm{corr}}\simeq 10$, the non-Markovian equations (denoted by NM) describe very accurately the dynamics although the Markovian ones (denoted by M) is exponential and deviate from the exact behavior. On a longer time scale (much longer than τ_{corr}), the solutions of the Markovian equations join those of the non-Markovian equations.

see that our equation always fits very well with the exact von Neumann equation, which is not the case of the Redfield equation. As argued before, this is due to the fact that the Redfield equation does not take into account the changes in the energy distribution of the environment induced by the system transitions. When the system energy is very small this makes almost no difference, but when it increases, this has to be taken into account and our master equation becomes necessary.

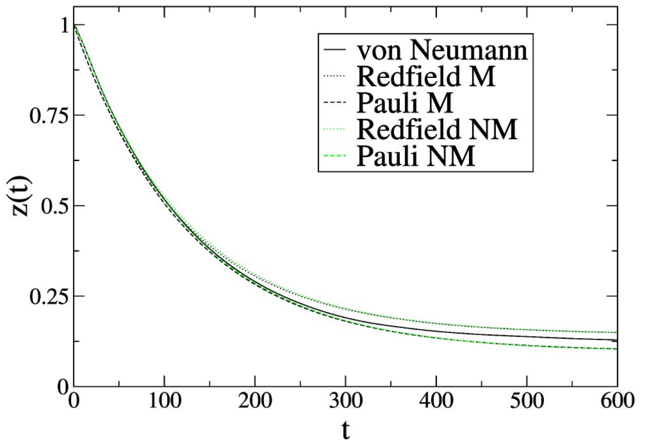

FIG. 7. Relaxation of the z component of the spin for the spin-GORM model for a small spin energy splitting $\Delta=0.1$ with $\lambda=0.1$, $\epsilon=0.25$, $N=2000$, and $\chi=10$. The exact solution of the von Neumann equation is compared with the solutions of the Pauli and Redfield Markovian (M) and non-Markovian (NM) equations. We see that our master equation (Pauli NM) gives the best results and that the solutions of the Markovian equations remain very close to those of the non-Markovian equations.

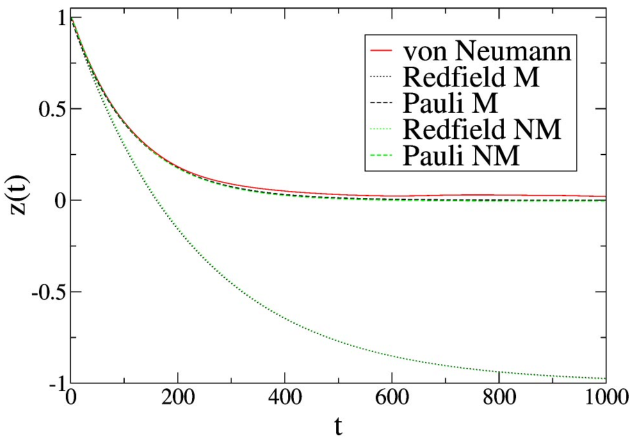

FIG. 8. Relaxation of the z component of the spin for the spin-GORM model for an intermediate spin energy splitting $\Delta=0.5$ with $\lambda=0.1$, $\epsilon=-0.25$, $N=2000$, and $\chi=10$. The exact solution of the von Neumann equation is compared with the solutions of the Pauli and Redfield Markovian (M) and non-Markovian (NM) equations. Here, we see that the Redfield equations give completely wrong results after a short time. The Pauli equations give much better results than the Redfield ones.

In particular, a large discrepancy happens for the solution of the Redfield equation in Fig. 8 although the solution of our master equation continues to be in agreement with the exact time evolution. This can be understand with Eqs. (106) and (115) for the asymptotic equilibrium values of the z component, which predict, respectively,

$$z_{\mathrm{Pauli}}=0, \tag{117}$$

$$z_{\mathrm{Redfield}}=-1, \tag{118}$$

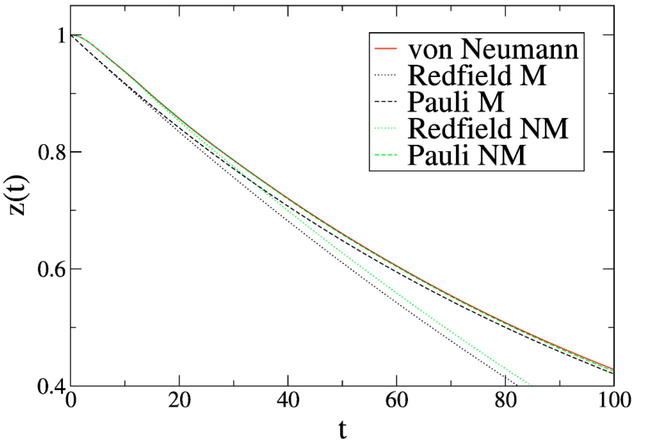

FIG. 9. Relaxation of the z component of the spin for the spin-GORM model in the same conditions $\Delta=0.5$, $\lambda=0.1$, $\epsilon=-0.25$, $N=2000$, and $\chi=10$ as in Fig. 8. We focus here on the short time dynamics in order to see that only the non-Markovian equations (NM) reproduce the initial behavior of the system which is not the case for the Markovian equations (M). After $\tau_{\mathrm{corr}}\simeq 10$, the non-Markovian Redfield equation (Redfield NM) becomes wrong but our master equation (Pauli NM) is still valid. On a longer time scale, the solution of the Markovian version of our master equation (Pauli M) joins the one of the non-Markovian version of our equation (Pauli NM).

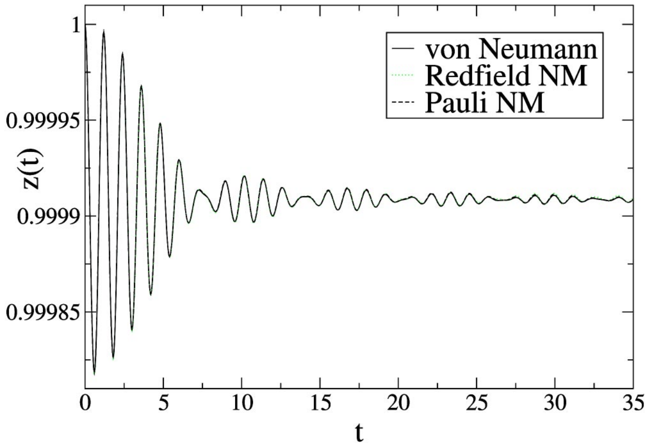

FIG. 10. Relaxation of the z component of the spin for the spin-GORM model for a large spin energy splitting $\Delta=5$ with $\lambda=0.1$, $\epsilon=0.25$, $N=2000$, and $\chi=10$. The exact solution of the von Neumann equation is compared with the solutions of the Pauli and Redfield non-Markovian (NM) equations. We are in a highly non-Markovian regime. The Markovian equations are not plotted here because their solutions are a constant equal to unity at all times and therefore miss the whole dynamics. We see that in this highly non-Markovian regime and on the short time scale τ_{corr} there is almost no difference between the non-Markovian Redfield equation (Redfield NM) and our master equation (Pauli NM).

for $\Delta=0.5$ and $\epsilon=-0.25$. The discrepancy of the Redfield equation finds its origin in the violation of energy conservation between the system and its environment by this equation. The Pauli equation has the advantage of allowing a correct energy exchange between the spin and its environment, which is crucial for obtaining the correct asymptotic equilibrium value of the z component.

We can also notice in Figs. 5, 7, and 8 that, on the global time scale, the non-Markovian and Markovian equations are very close to each other. But if we look on a shorter time scale, we see in Figs. 6 and 9 small differences between the non-Markovian and Markovian equations in the early stage of the decay. The solutions of the non-Markovian equations are in best agreement with the exact time evolution and present a nonexponential early decay on the time scale of the environment correlation time ($\tau_{\mathrm{corr}}\simeq 10$). In contrast, the solution of the Markovian equation immediately enters in an exponential decay and, thus slightly deviates from the exact solution. This observation concerns both the Redfield and Pauli equations. This suggests that, as explained in Refs. [11,12], a slippage of initial conditions is required for both Markovian equations in order to avoid this small early-decay discrepancy. We also observe that this discrepancy decreases with the energy splitting Δ. This is expected since the Markovian approximation is valid if the time scale of the system dynamics $2\pi/\Delta$ is longer than the environment time scale ($\tau_{\mathrm{corr}}\simeq 10$). Therefore, the smaller Δ is, the better is the Markovian approximation. If one wants to make a correct description of the system dynamics on a time scale of order τ_{corr}, the non-Markovian equations should be used (or the Markovian equations should be supplemented by a slippage of initial conditions [11,12]). We also see, in Fig. 9, that the Pauli non-Markovian equation gives better results than the Redfield non-Markovian equation not only on long time scales but also on short ones, even if their solutions essentially coincide on a very short time of order τ_{corr} but not more. Again, when the energy of the system is to small to affect the density of state of the environment, this difference between our non-Markovian equation and the Redfield non-Markovian equation disappears (see Figs. 6 and 9).

We see in Fig. 10 the relaxation of the z component of the spin in a highly non-Markovian regime. The energy difference between the two levels is here much larger than the width of the level density of the environment. The Markovian equations are not plotted here because they describe a constant value equal to unity for all times and, therefore, completely miss the dynamics. The whole spin dynamics happens on a time scale of order τ_{corr}. We also see that, in this highly non-Markovian regime, there is almost no difference between the non-Markovian Redfield equation and our master equation on the short time scale that we plotted. The non-Markovian Redfield equation as well as our non-Markovian master equation continue to fit with the exact dynamics even on longer time scales not represented here. The special structure seen in Fig. 10 can be understand by using Eqs. (109) and (110). Indeed, the curve is the result of some time integrations of the Bessel function $J_1(t/2)$ divided by t and modulated by $\cos\Delta t$. Since the modulations of $\cos\Delta t$ have a period $2\pi/\Delta$ shorter than the decay time $\tau_{\mathrm{corr}}\simeq 10$ of the Bessel function $J_1(t/2)$, a shape reminiscent of a Bessel function only appears as an envelope of the oscillations of the decay curve.

We conclude that, as expected from theoretical arguments, our master equation gives excellent predictions, especially in situations where the system energy is greater than or of the same order of magnitude as the typical energy scale of variation of the density of states of the environment. We also notice that for non-Markovian dynamics that happen on a time scale of order τ_{corr}, the non-Markovian Redfield equation gives the same result as our master equation for short time scales. But for longer time scales our equation is the only one that correctly describes the dynamics.

VI. CONCLUSIONS

We derived in this paper a master equation to study the dynamics of a quantum system interacting with its environment. This equation is obtained by a perturbative expansion with respect to the coupling parameter between the system and its environment. Our equation is more general than the previously obtained perturbative master equations because our equation explicitly takes into account the exchange of energy between the system and its environment. This effect is important when the density of state of the environment varies in a significant way on energy scales of the order of the system energy scales.

We showed how the well-known master equations of the literature can be derived from our equation (36) by performing different types of approximations. Our equation reduces to the non-Markovian Redfield equation (48) if one neglects the changes in the density of states of the environment induced by the system. Moreover, we showed that by performing the Markovian approximation on our equation and neglecting the coherence contribution to the population dynamics, we get a Pauli-type equation (42) for the total system (system+environment) that describes the time evolution in terms of distributions defined on the energy spectrum of the environment. When one neglects the changes in the energy distribution of the environment, the Markovian version of our equation (that is now equivalent to the Redfield equation) reduces to the master equation derived by Cohen-Tannoudji and co-workers in Ref. [5].

We have applied our equation to a two-level system interacting with a general environment (spin-environment model), especially, in the case where the environment operators are random matrices (spin-GORM model). In this case, we have carried out numerical simulations of the spin-GORM model (for which one can compute the exact solutions) that show the greater accuracy of our master equation with respect to the other well-known master equations in Markovian and non-Markovian situations.

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