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Relaxation of quantum systems weakly coupled to a bath. I. Total-time-ordering-cumulant and partial-time-ordering-cumulant non-Markovian theories

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The present paper studies the formal aspects of the total-time-ordering-cumulant (TTOC) and the partial-time-ordering-cumulant (PTOC) relaxations of a quantum system, of few degrees of freedom, in weak interaction with a bath, both within and outside the Markovian limit. To this end, the general expressions connecting the matrix elements of the TTOC and PTOC relaxation superoperators with the bath correlation functions are determined. Special attention is paid to two particular cases: a system with a nonequidistant energy spectrum and a system with an equidistant energy spectrum. Discussions revolve mainly around the possibility of applying the secular approximation to the TTOC and PTOC master equations for the off-diagonal matrix elements of the reduced-density operator of the system.

I. INTRODUCTION

There is extensive literature concerning the relaxation of a system, S, of a few degrees of freedom in weak interaction with another, B, whose number of degrees of freedom is much greater.[1–19] The physical situation is governed by two principal factors: (i) the weak interaction S-B, which introduces in S changes on a time scale that may be considered large relative to the rapid free time evolution of S; (ii) the high number of degrees of freedom of B, which allows us to assume that its statistical properties are not affected by the S-B interaction, consequently, behaving as a thermal bath for S. In this context the interaction S-B should induce a damping motion on S, i.e., an irreversible behavior that will terminate when S reaches statistical equilibrium with B.

There are two dynamical ways of attaining this goal. One stems from the Heisenberg equations of motion of the dynamical operators of the entire system $S \oplus B$.[20] The key behind this method lies in the consideration that due to the large number of degrees of freedom of the bath, any movement of S may be considered as a random motion. Averaging correctly on the bath operators leads us to a closed system of equations for the mean motion of the operators of S. Another way of tackling the problem is to start out from the Liouville equation for the density matrix $\rho(t)$, of the entire system $S \oplus B$.[21] In this instance the aim is to find the master equation which describes the time evolution of the statistical behavior of S. In both methods the effects of the bath on the motion of S appear in terms of certain time correlation functions.

In most approaches the time-evolution equations for the relaxation of S are obtained by making use of the Markovian hypothesis consisting of the assumption that the typical bath correlation times are zero when expressed on the time scale in which S is damped. This condition is not always fulfilled in practice, hence the interest in introducing formalisms leading to valid equations outside this limit.[17,18]

Another nontrivial problem is the integration of the equations for the irreversible motion of S. In fact, it is possible to arrive at analytical solutions only in a few particular cases, for example, those in which S is a two-level system[22] or a harmonic oscillator,[23] where it is normally assumed that the situation corresponds to the Markovian limit.

The object of the present paper is to discuss two different master equations for the evolution of the statistical behavior of S [described by its reduced-density matrix $\sigma(t)$] in a more general context than that of a two-level system or a system with consecutive coupled levels, in which they have already been used by Mukamel.[18] These equations are approximated to the second order in the interaction S-B.

Both the total-time-ordering-cumulant (TTOC) and partial-time-ordering-cumulant (PTOC) equations[13] are obtained without invoking the Markovian hypothesis by using two different temporal ordering prescriptions for Kubo's cumulant expansions.[13,17,18] Both formulations coincide at the Markovian limit, but outside it their predictions are different, and the greater suitability of one or the other will depend on the statistical properties of the bath.

For the sake of simplicity, we shall assume that the energy spectrum of S is nondegenerate. If there is no other restrictive constraint on this spectrum the TTOC and PTOC equations can be very complicated, since in these equations the evolution of each matrix element of $\sigma(t)$ is coupled to all the rest. Thus, once we have obtained the general expressions for the matrix elements of the TTOC and PTOC relaxation superoperators, our attention will be drawn to the study of certain situations of interest in which the problem is partially simplified, facilitating the understanding of the mechanisms which govern the properties of the damping of S.

In Sec. II we review the TTOC and PTOC master equations for $\sigma(t)$, independent of the energy spectrum of S. In the following, the Markovian TTOC and PTOC evolutions will be discussed separately, connecting the matrix elements of the corresponding relaxation superoperator with the bath correlation functions. Special attention is paid to the study of the time evolution of the coherences of $\sigma(t)$, the behavior of which determines the line shape in spectral problems.[19,24] The general formalism of these sections will allow us to study, either within or outside the Markovian limit, problems such as the vibrational relaxation or the rotational relaxation in condensed media or spin-lattice relaxation.

II. FORMULATION OF THE PROBLEM

We consider a small system S interacting weakly with a thermal bath B. The Hamiltonian of the entire system is

$$H=H_0+H'=H_S+H_B+H' , \tag{2.1}$$

H_S and H_B being, respectively, the Hamiltonians of the isolated systems S and B, and H' the Hamiltonian of the S-B interaction. We shall denote the eigenkets of H_0 as $|j\alpha\rangle$, $|j\rangle$ and $|\alpha\rangle$ being the eigenkets of H_S and H_B, respectively. For simplicity, they are assumed to be nondegenerate. We have the relations

$$H_0|j\alpha\rangle=(E_j+E_\alpha)|j\alpha\rangle , \quad |j\alpha\rangle\equiv|j\rangle\otimes|\alpha\rangle \tag{2.2a}$$

$$\sum_j\sum_\alpha |j\alpha\rangle\langle\alpha j|=\mathbb{1} , \tag{2.2b}$$

where $\mathbb{1}$ is the unity operator in the state space of $S\oplus B$.

In the $\{|j\alpha\rangle\}$ basis, H' can be written as

$$H'=\sum_{j,k}\sum_{\alpha,\beta}H'_{j\alpha,k\beta}|j,\alpha\rangle\langle\beta,k| , \tag{2.3a}$$

where

$$H'_{j\alpha,k\beta}=\langle\alpha,j|H'|k\beta\rangle\equiv\langle\alpha|H'_{jk}|\beta\rangle . \tag{2.3b}$$

In general $H'_{jk}=\langle j|H'|k\rangle$ are operators which depend only on the bath coordinates. When $j\neq k$, these operators will cause a coupling between the levels $|j\rangle$ and $|k\rangle$ of S, while when $j=k$, they will give rise to a shift of the E_j energies.

Let $\mathscr{L}$ be the Liouvillian of the complete system $S\oplus B$:[4,14,25]

$$\mathscr{L}X=\hbar^{-1}[H, x] . \tag{2.4}$$

Equation (2.1) allows us to write

$$\mathscr{L}=\mathscr{L}_0+\mathscr{L}'=\mathscr{L}_S+\mathscr{L}_B+\mathscr{L}' . \tag{2.5}$$

From Eqs. (2.2) and (2.3b), in the $\{|j\alpha,k\beta)\}$ basis of the total Liouville space,[26] we have

$$\begin{aligned}(\mathscr{L}_0)_{j\alpha,k\beta;l\gamma,m\xi}&=(j\alpha,k\beta|\mathscr{L}_0|l\gamma m\xi)\\&=(\omega_{jk}+\omega_{\alpha\beta})\delta_{jl}\delta_{km}\delta_{\alpha\gamma}\delta_{\beta\xi} ,\end{aligned} \tag{2.6a}$$

$$\begin{aligned}(\mathscr{L}')_{j\alpha,k\beta;l\gamma,m\xi}&=(j\alpha,k\beta|\mathscr{L}'|l\gamma,m\xi)\\&=\hbar^{-1}(H'_{j\alpha,l\gamma}\delta_{km}\delta_{\beta\xi}-H'_{m\xi,k\beta}\delta_{jl}\delta_{\alpha\gamma}) ,\end{aligned} \tag{2.6b}$$

with

$$\omega_{jk}=(E_j-E_k)/\hbar , \quad \omega_{\alpha\beta}=(E_\alpha-E_\beta)/\hbar , \tag{2.6c}$$

where we have made use of the Lynden-Bell notation[3] for the vectors of the Liouville space: $|ab)=|a\rangle\langle b|$.

The statistical description of system S is made by its reduced-density matrix

$$\sigma(t)=\mathrm{Tr}_B[\rho(t)] , \tag{2.7}$$

where $\rho(t)$ is the density matrix of the complete system $S\oplus B$ and Tr_B refers to the trace over the bath coordinates. We assume that at time $t=0$ the interaction H' does not affect the statistical distribution and, therefore, $\rho(0)$ can be written as a product of two factors

$$\rho(0)=\sigma(0)\rho_B^0 , \tag{2.8}$$

i.e., at the initial time the small system and the bath are uncorrelated, $\sigma(0)$ being the density matrix of S at $t=0$ and ρ_B^0 the equilibrium density matrix of the bath.

Finally, we have assumed that the splitting of Eq. (2.5) for $\mathscr{L}$ is such that

$$\langle\mathscr{L}'\rangle\equiv\mathrm{Tr}_B(\mathscr{L}'\rho_B^0)=0 , \tag{2.9}$$

which can always be achieved by redefining $\mathscr{L}_S$ and $\mathscr{L}'$ in a suitable form. In the following $\langle\ \rangle$ means the bath average.

Using the Liouville formalism, we can write[7,13,18]

$$\sigma(t)=e^{-i\mathscr{L}_St}\langle\hat{A}(t)\rangle\sigma(0) , \tag{2.10}$$

where

$$\begin{aligned}\hat{A}(t)&=\exp_{-t}\left[-i\int_0^t d\tau\,\tilde{\mathscr{L}}'(\tau)\right]\\&\equiv\hat{1}+(-i)\int_0^t dt_1\tilde{\mathscr{L}}'(t_1)+(-i)^2\int_0^t dt_1\int_0^{t_1}dt_2\tilde{\mathscr{L}}'(t_1)\tilde{\mathscr{L}}'(t_2)+\dots\\&\quad+(-i)^n\int_0^t dt_1\dots\int_0^{t_{n-1}}dt_n\tilde{\mathscr{L}}'(t_1)\dots\tilde{\mathscr{L}}'(t_n)+\dots ,\end{aligned} \tag{2.11a}$$

$$\tilde{\mathscr{L}}'(t)=e^{i\mathscr{L}_0t}\mathscr{L}'e^{-i\mathscr{L}_0t} \quad \text{with } \mathscr{L}'\equiv\mathscr{L}'(0) . \tag{2.11b}$$

The time-evolution superoperator $\langle \hat{A}(t) \rangle$ can be written using the Kubo cumulant expansion.[27,28] The choice of the different temporal ordering prescriptions for this expansion leads to different master equations for $\sigma(t)$. In Eq. (2.11), the superoperators $\tilde{\mathscr{L}}'(t)$ are arranged in decreasing value of the parameter t. We consider, in particular, a total ordering prescription and a partial ordering prescription, by truncating the expansion in the second order of the S-B interaction. This gives[13,18,29] the following.

(i) The TTOC master equation

$$\dot{\sigma}(t) = -i\mathscr{L}_S\sigma(t) - \int_0^t d\tau\, \hat{W}(t-\tau)\sigma(\tau) , \tag{2.12}$$

where

$$\hat{W}(t) = \langle \mathscr{L}'(t) e^{-i\mathscr{L}_S t} \mathscr{L}' \rangle , \tag{2.13a}$$

$$\mathscr{L}'(t) = e^{i\mathscr{L}_B t} \mathscr{L}' e^{-i\mathscr{L}_B t} . \tag{2.13b}$$

(ii) The PTOC master equation

$$\dot{\sigma}(t) = -i\mathscr{L}_S\sigma(t) - \hat{K}(t)\sigma(t) , \tag{2.14}$$

where

$$\hat{K}(t) = \int_0^t d\tau\, \hat{W}(t) e^{i\mathscr{L}_S t} . \tag{2.15}$$

In the Markovian limit, which assumes that the bath correlation time t_c is practically zero on the time scale of the damping of $\sigma(t)$, both equations (2.13) and (2.15) have the same form:

$$\dot{\sigma}(t) = -i\mathscr{L}_S\sigma(t) - \hat{R}\sigma(t) , \tag{2.16}$$

where

$$\hat{R} = \hat{K}(\infty) = \int_0^\infty dt\, \hat{W}(t) e^{i\mathscr{L}_S t} . \tag{2.17}$$

III. MARKOVIAN EVOLUTION

In the representation of the eigenstates of H_S, Eq. (2.16) takes the form

$$\dot{\sigma}_{jk}(t) = -i\omega_{jk}\sigma_{jk}(t) - \sum_{l,m} \hat{R}_{jk,lm}\sigma_{lm}(t) . \tag{3.1}$$

From Eqs. (2.17) and (A8), the matrix elements of the superoperator $\hat{R}$, which determine the relaxation properties of S in the Markovian limit, are related to its natural frequencies and to the bath correlation functions

$$\langle H'_{pq}(t) H'_{rs} \rangle = \mathrm{Tr}_B[H'_{pq}(t) H'_{rs}] = \sum_{\alpha,\beta} \rho_B^0(\alpha) e^{i\omega_{\alpha\beta}t} H'_{p\alpha,q\beta} H'_{r\beta,s\alpha} \tag{3.2}$$

by the expressions

$$\hat{R}_{jk,lm} = \int_0^\infty dt\, e^{i\omega_{lm}t} \hat{W}_{jk,lm}(t) = \overline{\hat{W}}_{jk,lm}(\omega_{lm}) = \delta_{km} \sum_n J_{jn,nl}(\omega_{\mathrm{ln}}) + \delta_{jl} \sum_n J^*_{kn,nm}(\omega_{mn}) - J_{mk,jl}(\omega_{lj}) - J^*_{lj,km}(\omega_{mk}) \tag{3.3a}$$

with

$$J_{pq,rs}(\omega) = \int_0^\infty dt\, e^{i\omega t} \langle H'_{pq}(t) H'_{rs} \rangle . \tag{3.3b}$$

Note that

$$\langle H'_{pq}(t) H'_{rs} \rangle^* = \langle H'_{sr} H'_{qp}(t) \rangle . \tag{3.4}$$

When H' is known, the incorporation of the bath correlation functions $\langle H'_{pq}(t) H'_{rs} \rangle$ into the problem may be performed either by calculating them from a dynamic model for the bath or directly from a stochastic description for the bath.

We now take the Laplace-Fourier transformation, defined by

$$\bar{f}(\omega) = \int_0^\infty dt\, e^{i\omega t} f(t) \tag{3.5}$$

in Eq. (3.1), obtaining

$$\omega\bar{\sigma}_{jk}(\omega) - i\sigma_{jk}(0) = \omega_{jk}\bar{\sigma}_{jk}(\omega) - i\sum_{l,m} \hat{R}_{jk,lm}\bar{\sigma}_{lm}(\omega) . \tag{3.6}$$

Owing to the presence of the interference terms for $\hat{R}_{jk,lm}\bar{\sigma}_{lm}(\omega)$, with $(j,k) \neq (l,m)$, a solution for $\sigma_{jk}(t)$ from Eq. (3.6) is, except in particularly simple cases (such as the two-level system), a nontrivial problem which in general should be tackled by techniques of numerical calculus. Note, Eq. (3.3), that if H' is diagonal, the only nonzero matrix elements of $\hat{R}$ are $\hat{R}_{jk,jk}$ with $j \neq k$. Thus, in this particular case, the relaxation of each coherence takes place independently of the others, and the populations remain constant.

Without such a restrictive condition in H', Eq. (3.1) undergoes a noticeable simplification when the nonsecular terms of the right-hand side (rhs) are negligible, that is, those terms which mix the time evolution of the matrix elements $\sigma_{jk}(t)$ with those of $\sigma_{lm}(t)$ such that, in the free evolution of S, they oscillate with a different frequency than ω_{jk} (Ref. 5) (in the case of populations $\omega_{jk}=0$).

From a qualitative point of view the interaction S-B implies a broadening, with respect to free evolution, of the spectral functions $\bar{\sigma}_{lm}(\omega)$. Though the condition of weak interaction implies that this broadening should not be excessively large compared with the mean spacing between the natural frequencies of S, this condition does not necessarily avoid the overlapping between spectral functions $\bar{\sigma}_{lm}(\omega)$ corresponding to neighboring frequencies. In general, the neglect of nonsecular terms, of the kind of $\hat{R}_{jk,lm}\bar{\sigma}_{lm}(\omega)$, in Eq. (3.6) is justified when the overlapping between neighboring spectral functions $\bar{\sigma}_{lm}(\omega)$ is negligible and the coupling coefficients $\hat{R}_{jk,lm}$ are small though, usually, the condition of negligible overlap implies very small coupling coefficients and vice versa.

A sufficient condition for applying the secular approximation is that the interaction S-B should be sufficiently weak for the fulfillment of the relationships

$$|\omega_{jk} - \omega_{lm}| \gg |\hat{R}_{jk,jk}| , |\hat{R}_{lm,lm}| , \quad |\omega_{jk} - \omega_{lm}| \gg |\hat{R}_{jk,lm}| , \tag{3.7}$$

with $(j,k)\neq(l,m)$. The properties of S are, therefore, conditioned by the relaxation superoperator and by the spacings between its natural frequencies. [Note that the terms of the rhs of Eq. (3.6) with indices (j,k,l,m) such that $\omega_{jk}=\omega_{lm}$, do not verify condition (3.7) and, therefore, they cannot be ignored. In particular, the secular approximation does not allow uncoupling between populations.]

We shall now consider two kinds of spectra of H_S which lead to particularly interesting situations, the study of which makes the understanding of more complicated ones easier.

A. System with nonequidistance energy spectrum

Let us now assume a spectrum of H_S with more than two levels, spaced in such a way that all its natural frequencies are different. The application of the secular approximation to Eq. (3.6) allows us to write, for coherences and populations, the multilevel Bloch equations[18]

$$\omega\bar{\sigma}_{jk}(\omega)-i\sigma_{jk}(0)=(\tilde{\omega}_{jk}-i\Gamma_{jk})\bar{\sigma}_{jk}(\omega)\ , \tag{3.8a}$$

$$\omega\bar{\sigma}_{jj}(\omega)-i\sigma_{jj}(0)=-i\Gamma_j\bar{\sigma}_{jj}(\omega)-i\sum_{k\,(\neq j)}\gamma_{jk}\bar{\sigma}_{kk}(\omega)\ , \tag{3.8b}$$

with

$$\tilde{\omega}_{jk}=\omega_{jk}-\Delta_{jk}\ , \tag{3.9a}$$

$$\Delta_{jk}=\mathrm{Im}(\hat{R}_{jk,jk})=\mathrm{Im}\left[\sum_{n\,(\neq j)}J_{jn,nj}(\omega_{jn})+\sum_{n\,(\neq k)}J^{*}_{kn,nk}(\omega_{kn})\right]+i\frac{\hbar^2}{2}\int_0^\infty dt\langle[H'_{jj}(t)-H'_{kk}(t)\,,H'_{jj}-H'_{kk}]\rangle\ , \tag{3.9b}$$

$$\Gamma_{jk}=\mathrm{Re}(\hat{R}_{jk,jk})=\frac{\hbar^2}{2}\sum_{n\,(\neq j)}\int_{-\infty}^{+\infty}dt\,e^{i\omega_{jn}t}\langle H'_{jn}(t)H'_{nj}\rangle+\frac{\hbar^2}{2}\sum_{n\,(\neq k)}\int_{-\infty}^{+\infty}dt\,e^{i\omega_{kn}t}\langle H'_{kn}(t)H'_{nk}\rangle$$
$$+\frac{\hbar^2}{2}\int_0^\infty dt\langle[H'_{jj}(t)-H'_{kk}(t)\,,H'_{jj}-H'_{kk}]_+\rangle\ , \tag{3.9c}$$

$$\gamma_{jk}=\hat{R}_{jj,kk}=-\hbar^{-2}\int_{-\infty}^{+\infty}dt\,e^{i\omega_{kj}t}\langle H'_{kj}(t)H'_{jk}\rangle\ , \tag{3.9d}$$

$$\Gamma_j=\hat{R}_{jj,jj}=\hbar^2\sum_{k\,(\neq j)}\int_{-\infty}^{+\infty}dt\,e^{i\omega_{jk}t}\langle H'_{jk}(t)H'_{kj}\rangle=-\sum_{k\,(\neq j)}\gamma_{kj}\ . \tag{3.9e}$$

According to Eq. (3.8b), the relaxation of the populations are coupled with each other, and we cannot expect to find an analytical simple solution. This is undertaken either by numerical calculus techniques or by making suitable hypotheses which will allow us to make the problem analytically soluble.[10,30]

As far as coherences are concerned, from Eq. (3.8a) we have

$$\bar{\sigma}_{jk}(\omega)=\frac{i\sigma_{jk}(0)}{\omega-\tilde{\omega}_{jk}+i\Gamma_{jk}}\ , \tag{3.10}$$

and taking the inverse Laplace-Fourier transformation

$$\sigma_{jk}(t)=\sigma_{jk}(0)e^{-i\tilde{\omega}_{jk}t}e^{-\Gamma_{jk}t}\ . \tag{3.11}$$

That is, if the secular approximation is applicable, each coherence will evolve independently of the others. According to Eq. (3.11), the bath induces in the coherences (or phases) a slight frequency shift Δ_{jk} and a damping with a dephasing time

$$(T_2)_{jk}=(\Gamma_{jk})^{-1}\ . \tag{3.12}$$

It is interesting to apply these results to a two-level system in the secular approximation, already treated in the literature.[18(a)] In this case, indices j,k of Eq. (3.8) can only take the values 1 or 2 and Eq. (3.8) leads to

$$\bar{\sigma}_{ab}(\omega)=\frac{i\sigma_{ab}(0)}{\omega-\omega_{ab}+i\Gamma_{ab}}\ , \tag{3.13a}$$

$$\bar{\sigma}_{aa}(\omega)=\frac{i\omega\sigma_{aa}(0)-\Gamma_b}{\omega[\omega+i(\Gamma_a+\Gamma_b)]}\ , \tag{3.13b}$$

where $a,b=1,2$, with $a\neq b$, and where use has been made of the relationship (A10)

$$\hat{R}_{bb,bb}=-\hat{R}_{aa,aa}\ . \tag{3.14}$$

From Eq. (3.13), we have

$$\sigma_{ab}(t)=\sigma_{ab}(0)e^{-i\tilde{\omega}_{ab}t}e^{-\Gamma_{ab}t}\ , \tag{3.15a}$$

$$\sigma_{aa}(t)=\frac{\Gamma_b}{\Gamma_a+\Gamma_b}+\left[\sigma_{aa}(0)-\frac{\Gamma_b}{\Gamma_a+\Gamma_b}\right]e^{-(\Gamma_a+\Gamma_b)t}\ . \tag{3.15b}$$

It is interesting to point out that Eq. (3.15b) says that for a two-level system in the secular approximation each population decays independently, without a frequency shift, with a decay time

$$T_1=(\Gamma_a+\Gamma_b)^{-1}\ . \tag{3.16}$$

Note that making use of the relationship[31]

$$\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\langle A(t)B\rangle=e^{\hbar\omega/Tk_B}\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}\langle B(t)A\rangle\ , \tag{3.17}$$

valid for any two bath operators A and B if the bath is at a temperature T, we have

$$\sigma_{aa}(\infty)=\frac{\Gamma_a}{\Gamma_a+\Gamma_b}=(e^{\hbar\omega_{ab}/Tk_B}+1)^{-1}\ , \tag{3.18}$$

which are the populations of a two-level system in thermal equilibrium. Since $\Gamma_{ab}=\Gamma_{ba}$, both coherences decay with the same dephasing time

$$T_2=(\Gamma_{ab})^{-1} . \tag{3.19}$$

Comparing Eqs. (3.9c) and (3.9e), we have for a two-level system

$$\Gamma_{ab}=\tfrac{1}{2}(\Gamma_a+\Gamma_b)+\Gamma_{ab}^{\text{ph}} , \tag{3.20}$$

where

$$\Gamma_{ab}^{\text{ph}}=\Gamma_{ba}^{\text{ph}} =\tfrac{1}{2}\hbar^{-2}\int_0^t dt\langle[H'_{aa}(t)-H'_{bb}(t),H'_{aa}-H'_{bb}]_+\rangle . \tag{3.21}$$

Equation (3.20) may be written now as

$$(T_2)^{-1}=(2T_1)^{-1}+(T_2^{\text{ph}})^{-1} , \tag{3.22}$$

where

$$T_2^{\text{ph}}=(\Gamma_{ab}^{\text{ph}})^{-1} . \tag{3.23}$$

If H' is diagonal, from Eq. (3.9e) we see that $\Gamma_a=0$ and the damping of S consists of a pure dephasing. Then Eq. (3.22) adopts the form

$$T_2=T_2^{\text{ph}} \text{ for diagonal } H' . \tag{3.24}$$

For this reason, T_2^{ph} is generally called the pure dephasing time. If, however, H' is nondiagonal, from Eq. (3.21) we have $\Gamma_{ab}^{\text{ph}}=0$, and Eq. (3.22) yields in this case

$$T_2=2T_1 \text{ for nondiagonal } H' . \tag{3.25}$$

The relative magnitudes of T_1 and T_2 for the vibrational relaxation in condensed media (in the two-level approximation) are discussed in Refs. 15 and 32–34. For the relaxation T_1 and T_2 of a spin system in different media, see Ref. 35.

Comparing Eqs. (3.9c) and (3.9e), we have in the general case

$$\Gamma_{jk}=\tfrac{1}{2}(\Gamma_j+\Gamma_k)+\Gamma_{jk}^{\text{ph}} , \tag{3.26}$$

where

$$\Gamma_{jk}^{\text{ph}}=\frac{h^{-2}}{2}\int_0^\infty dt\langle[H'_{jj}(t)-H'_{kk}(t),H'_{jj}-H'_{kk}]_+\rangle . \tag{3.27}$$

Equation (3.22), relative to a two-level system, suggests the possibility of writing Eq. (3.26) as

$$(T_2)_{jk}^{-1}=(2T_1)_{jk}^{-1}+(T_2^{\text{ph}})_{jk}^{-1} . \tag{3.28}$$

The parameters $(T_2)_{jk}$ and $(T_2^{\text{ph}})_{jk}$ are still interpretable in this equation, as in the two-level case, as the dephasing times associated with the coherence $\sigma_{jk}(t)$. However, $(T_1)_{jk}$ is not directly interpretable as a damping time of populations. It should also be noted that if the mixing between coherences becomes significant, Eq. (3.11) is no longer valid for the loss of phase, and a nonexponential behavior appears, which requires a new interpretation. In Secs. IV and V we shall discuss this problem in the more general context of the TTOC and PTOC evolutions.

In the case of a two-level system it is quite clear that the sufficient conditions (3.7) imply the secular approximation. Indeed, in agreement with Eq. (3.13a), the spectral function $\bar{\sigma}_{ab}(\omega)$ will only take appreciable values in a frequency range of the order $\Gamma_{ab}=\text{Re}(\hat{R}_{ab,ab})$ around $\tilde{\omega}_{ab}$ (in fact, slightly shifted with respect to ω_{ab} [Eq. (3.9a)]), while $\tilde{\sigma}_{aa}(\omega)$, according to Eq. (3.13b), will only take non-negligible values in a frequency range of the order of $\Gamma_a+\Gamma_b=\hat{R}_{aa,aa}+\hat{R}_{bb,bb}$ around $\omega=0$. Therefore, conditions (3.7) guarantee at the same time that these functions do not overlap each other and that the corresponding coupling coefficients do not give rise to significant interferences (the possibility of overlapping between the two coherences is even smaller).

B. Systems with equidistant energy spectrum

When the difference between the energy of two consecutive levels of S is constant, we face a situation of a different nature than that of the nonequidistant case.[10,36] This happens, for example, with the harmonic oscillator or with a spin in a magnetic field.

The frequencies ω_{lm} are now multiples of the frequency ω_0, associated with two consecutive levels: $\omega_{lm}=(l-m)\omega_0$. Thus, the conditions (3.7) are no longer verified for all the frequencies ω_{lm} such that $l-m=j-k$. The secular approximation, which here allows us to uncouple only those coherences for which $l-m\neq j-k$, yields, separating coherences and populations,

$$\omega\bar{\sigma}_{jk}(\omega)-i\sigma_{jk}(0) =(\omega_{jk}-i\hat{R}_{jk,jk})\bar{\sigma}_{jk}(\omega) -i\sum_{\substack{l,m\\(l,m)\neq(j,k)}}\hat{R}_{jk,lm}\bar{\sigma}_{lm}(\omega) , \tag{3.29a}$$

$$\omega\bar{\sigma}_{jj}(\omega)-i\sigma_{jj}(0) =-i\hat{R}_{jj,jj}\bar{\sigma}_{jj}(\omega)-i\sum_{k\,(\neq j)}\hat{R}_{jj,kk}\bar{\sigma}_{kk}(\omega) , \tag{3.29b}$$

where the sum in Eq. (3.29a) is restricted to the indices (l,m) for which $l-m=j-k$.

A similar situation may be found in the case of degenerate levels,[9,10] as happens, for example, in the rotational relaxation of a diatomic molecule where $|k\rangle$ now designates the states of the quantum rotation $|j_k m_k\rangle$. In this case, the evolution of the coherences will be given by an equation analogous to Eq. (3.29a), where the sum would be extended to all indices m_k and $m_{k'}$ corresponding, respectively, to the degenerate states with energies E_k and $E_{k'}$. As far as the time evolution of the populations is concerned, it would be necessary to take into account the nonresonant contributions coming from the degenerated states with the same energy. Therefore, from a formal point of view, the treatment in the case of degeneration is similar to that of the nondegenerate one, except that the sums over the indices will be more complex.

IV. THE TTOC EVOLUTION

In the representation of the eigenstates of H_S, Eq. (2.12) takes the form of

$$\dot{\sigma}_{jk}(t)=-i\omega_{jk}\sigma_{jk}(t)-\sum_{l,m}\int_0^t d\tau\,\hat{W}_{jk,lm}(t-\tau)\sigma_{lm}(\tau)\,, \tag{4.1}$$

where (see the Appendix)

$$\hat{W}_{jk,lm}(t)=\hbar^2\left[\delta_{km}\sum_n e^{-i\omega_{nk}t}\langle H'_{jn}(t)H'_{nl}\rangle+\delta_{jl}\sum_n e^{-i\omega_{jn}t}\langle H'_{mn}H'_{nk}(t)\rangle-e^{-i\omega_{jm}t}\langle H'_{mk}(t)H'_{jl}\rangle-e^{-i\omega_{lk}t}\langle H'_{mk}H'_{jl}(t)\rangle\right]. \tag{4.2}$$

The convolution integral in Eq. (4.1) suggests that we take the Laplace-Fourier transformation

$$\omega\bar{\sigma}_{jk}(\omega)-i\sigma_{jk}(0)=\omega_{jk}\bar{\sigma}_{jk}(\omega)-i\sum_{l,m}\bar{\hat{W}}_{jk,lm}(\omega)\bar{\sigma}_{lm}(\omega)\,, \tag{4.3}$$

where [Eqs. (3.3) and (4.2)]

$$\begin{aligned}\bar{\hat{W}}_{jk,lm}(\omega)&=\int_0^\infty dt\,e^{i\omega t}\hat{W}_{jk,lm}(t)\\&=\delta_{km}\sum_n J_{jn,nl}(\omega-\omega_{nk})+\delta_{jl}J^*_{kn,nm}(\omega_{jn}-\omega)\\&\quad-J_{mk,jl}(\omega-\omega_{jm})-J^*_{lj,km}(\omega_{lk}-\omega)\,.\end{aligned} \tag{4.4}$$

The difference between Eq. (4.3) and the Markovian equation (3.6) lies in the fact that the matrix elements $\bar{\hat{W}}_{jk,lm}(\omega)$, which determine the TTOC relaxation properties of S now depend on ω. As in the Markovian case, if H' is diagonal, the only nonzero matrix elements of the superoperator $\bar{\hat{W}}(\omega)$ are [Eq. (4.4)] $\bar{\hat{W}}_{jk,jk}$ with $j\neq k$, and, therefore, in this case the evolution of each coherence is independent while the populations remain constant.

For the sake of illustration of the analytical behavior of $\bar{\hat{W}}_{jk,lm}(\omega)$, we suppose that H' can be written as a product of factors

$$H'=\hbar VF\,, \tag{4.5}$$

where V and F are, respectively, operators of S and B. [Usually H' is given as a sum of terms of the same kind as those in Eq. (4.5)]. We shall also assume that the autocorrelation function of F is exponential with a decay time t_0, such that

$$\begin{aligned}\langle H'_{pq}(t)H'_{rs}\rangle&=\hbar^2V_{pq}V_{rs}\langle F(t)F\rangle\\&=\hbar^2|c|^2V_{pq}V_{rs}e^{-|t|/t_0}\,,\end{aligned} \tag{4.6}$$

where $|c|^2$ is a parameter which describes the contribution of the operator F to the intensity of the interaction S-B.

The substitution of Eq. (4.6) in Eq. (3.3) yields

$$J_{pq,rs}(\omega-\omega_{jk})=|c|^2V_{pq}V_{rs}\frac{t_0^{-1}+i(\omega-\omega_{jk})}{(\omega-\omega_{jk})+t_0^{-2}}\,, \tag{4.7}$$

which shows that this function takes appreciable values in a frequency range of the order of t_0^{-1} around the frequency ω_{jk}. The dependence of the real and imaginary parts of Eq. (4.7) on ω will be smoother (sharper) the smaller (bigger) the value of t_0, and making use of Eq. (4.4) we shall find a similar behavior for the matrix elements $\bar{\hat{W}}_{jk,lm}(\omega)$. In this case t_0 plays the role of the bath correlation time.

Normally the temporal dependence of the correlation function $\langle H'_{pq}(t)H'_{rs}\rangle$ is not as simple as expressed in Eq. (4.6). However, its analytical form, which will depend on the indices (p,q,r,s), will still be damped and characterized by the corresponding correlation times. Therefore, the functions $\bar{\hat{W}}_{jk,lm}(\omega)$ will be smoother the smaller these correlation times become.

A. Secular approximation

In the TTOC evolution the secular approximation will be guaranteed by fulfilling the sufficient conditions [with $(j,k)\neq(lm)$]

$$\begin{aligned}|\omega_{jk}-\omega_{lm}|&\gg|\bar{\hat{W}}_{jk,jk}(\omega)|\,,\;|\bar{\hat{W}}_{lm,lm}(\omega)|\,,\\|\omega_{jk}-\omega_{lm}|&\gg\bar{\hat{W}}_{jk,lm}(\omega)|\end{aligned} \tag{4.8}$$

in the region of ω where the $\bar{\sigma}_{lm}(\omega)$ take significant values. Note that, if the relaxation of S takes place in conditions not too far from the Markovian limit, the dependence on ω of the functions $\bar{\hat{W}}_{jk,lm}(\omega)$ must be relatively smooth, and $\bar{\hat{W}}_{jk,lm}(\omega)\simeq\bar{\hat{W}}_{jk,lm}(\omega_{lm})=\hat{R}_{jk,lm}$ [Eq. (3.3a)].

For a system with a nonequidistant energy spectrum, if in Eq. (4.3) the nonsecular terms are neglected, one obtains, separating coherences and populations,

$$\omega\bar{\sigma}_{jk}(\omega)-i\sigma_{jk}(0)=[\omega_{jk}-i\bar{\hat{W}}_{jk,jk}(\omega)]\bar{\sigma}_{jk}(\omega)\,, \tag{4.9a}$$

$$\omega\bar{\sigma}_{jj}(\omega)-i\sigma_{jj}(0)=-i\bar{\hat{W}}_{jj,jj}(\omega)\bar{\sigma}_{jj}(\omega)-i\sum_{k\,(\neq j)}\bar{\hat{W}}_{jj,kk}(\omega)\bar{\sigma}_{kk}(\omega)\,. \tag{4.9b}$$

Therefore, while the evolution of each coherence is independent, the population relaxation continues to be a nontrivial problem that it is necessary to solve in each individual case.

From Eq. (4.9a), one obtains

$$\bar{\sigma}_{jk}(\omega)=\frac{i\sigma_{jk}(0)}{\omega-\omega_{jk}+i\bar{\hat{W}}_{jk,jk}(\omega)}\,. \tag{4.10}$$

Once the analytical form of $\bar{\hat{W}}_{jk,jk}(\omega)$ is known, the inverse Laplace-Fourier transformation of Eq. (4.10) solves the problem of the TTOC phase relaxation within the secular approximation.

For frequencies such that $|\omega-\omega_{jk}| \ll t_c^{-1}$, where t_c is the bath correlation time, we can write $\exp[i(\omega-\omega_{lm})t]\simeq 1$ in the integral of Eq. (4.4), and, therefore, the function $\overline{\widehat{W}}_{jk,jk}(\omega)$ remains practically equal to $\overline{\widehat{W}}_{jk,jk}(\omega_{jk})$. Thus, in this frequency range, Eq. (4.10) takes the form

$$\bar{\sigma}_{jk}(\omega)=\frac{i\sigma_{jk}(0)}{\omega-\omega_{jk}+i\overline{\widehat{W}}_{jk,jk}(\omega_{jk})} \tag{4.11}$$

and, taking into account that according to Eq. (3.3a) $\overline{\widehat{W}}_{jk,jk}(\omega_{jk})=\widehat{R}_{jk,jk}$, this equation is identical to Eq. (3.10), valid in the Markovian limit. In this context, it is of interest to discuss the domain of validity of the Markovian hypothesis. According to Eqs. (4.11) and (3.9c) the real and imaginary parts of the function $\bar{\sigma}_{jk}(\omega)$ will have values appreciably different from zero in a range such that $|\omega-\omega_{jk}| \lesssim \Gamma_{jk}$ and, therefore, if

$$\Gamma_{jk} \ll t_c^{-1} \tag{4.12}$$

is verified, $\bar{\sigma}_{jk}(\omega)$ will be given by Eq. (4.11) in the frequency range of interest. Hence, the relationship (4.12) gives the condition of validity of the hypothesis of Markovian evolution for $\sigma_{jk}(t)$.

In view of the relationship (4.12), it is clear that there are two factors which contribute to the Markovian limit for $\sigma_{jk}(t)$: (a) a sufficiently weak coupling and (b) a very small bath correlation time. Note that a sufficiently weak coupling guarantees both condition (4.12) and the nonoverlapping of the coherence. However, this nonoverlapping of the coherences is not implied by the absence of correlation of the bath. In other words, in the Markovian limit, the secular approximation can be nonvalid, though both approximations are justified in the limit of weak coupling.

When Γ_{jk} approaches the order of magnitude of t_c^{-1}, the dependency of $\overline{\widehat{W}}_{jk,jk}(\omega)$ on ω may become important in Eq. (4.10), and Eq. (4.11) is no longer applicable. In the regions in which $|\overline{\widehat{W}}_{jk,jk}(\omega)| \ll |\omega-\omega_{jk}|$ we may carry out in Eq. (4.10) a series expansion in powers of $\overline{\widehat{W}}(\omega)$ and, retaining only the first-order term, we obtain

$$\bar{\sigma}_{jk}(\omega)=\frac{i\sigma_{jk}(0)}{\omega-\omega_{jk}}\left[1+\frac{i\overline{\widehat{W}}_{jk,jk}(\omega)}{\omega-\omega_{jk}}\right], \tag{4.13}$$

which gives the behavior in the "wings" within the secular approximation.

B. Mixing between coherences

The secular approximation is inadequate when the mean widths of the spectral functions $\bar{\sigma}_{lm}(\omega)$ and the coupling coefficients approach or exceed the mean spacings between the natural frequencies of S. In the particular case of a system with a nonequidistant spectrum, if the overlapping between the spectral functions associated to a certain set of coherences (for example, the coherences of a positive spectrum) are not negligible (even if they are small), the problem of its evolution can be tackled by an iterative method. Taking Eq. (4.10) as the zeroth-order solution we have, for the first order in the iterative process, the solutions

$$\bar{\sigma}_{jk}(\omega)=\frac{1}{\omega-\omega_{jk}+i\overline{\widehat{W}}_{jk,jk}(\omega)}\times\left[i\sigma_{jk}(0)+\sum_{\substack{l,m\\(l,m)\neq(j,k)}}\frac{\overline{\widehat{W}}_{jk,lm}(\omega)\sigma_{lm}(0)}{\omega-\omega_{lm}+i\overline{\widehat{W}}_{lm,lm}(\omega)}\right], \tag{4.14}$$

where the terms which most contribute to the sum will be those for which ω_{lm} is close to ω_{jk}.

A phenomenon of certain importance in the low-frequency range is that the populations and the negative and positive coherences can be mutually influenced and the problem of their time evolution can become more complex.

V. THE PTOC EVOLUTION

Except in the Markovian limit in which they both coincide, the solution of the TTOC and PTOC evolution presents different mathematical problems which should be discussed independently. In the representation of the eigenstates of H_S, Eq. (2.14) takes the form of

$$\dot{\sigma}_{jk}(t)=-i\omega_{jk}\sigma_{jk}(t)-\sum_{l,m}\widehat{K}_{jk,lm}(t)\sigma_{lm}(t), \tag{5.1}$$

where, taking into account Eqs. (2.15) and (4.2), the matrix elements of the PTOC relaxation superoperator are related to the natural frequencies of system S and to the correlation functions $\langle H'_{pq}(t)H'_{rs}\rangle$ by

$$\begin{aligned}\widehat{K}_{jk,lm}(t)&=\int_0^t d\tau\, e^{i\omega_{lm}\tau}\overline{\widehat{W}}_{jk,lm}(\tau)\\&=\delta_{km}\sum_n G_{jn,nl}(t)+\delta_{jl}\sum_n G^*_{kn,nm}(t)\\&\quad-G_{mk,jl}(t)-G^*_{lj,km}(t),\end{aligned} \tag{5.2}$$

with

$$G_{pq,rs}(t)=\hbar^{-2}\int_0^t d\tau\, e^{-i\omega_{rs}\tau}\langle H'_{pq}(\tau)H'_{rs}\rangle. \tag{5.3}$$

Comparing Eqs. (3.3) and (5.3) we have, in particular, the relationship

$$G_{pq,rs}(\infty)=J_{pqrs}(\omega_{sr}), \tag{5.4}$$

and therefore

$$\widehat{K}_{jk,lm}(\infty)=\widehat{R}_{jk,lm}. \tag{5.5}$$

As an illustration of the behavior of the functions $\widehat{K}_{jk,lm}(t)$, we shall reconsider the case in which the bath correlation functions $\langle H'_{pq}(t)H'_{rs}\rangle$ are of the form of Eq. (4.6). Substituting Eq. (4.6) in Eq. (5.3), we have

$$G_{pq,rs}(t)=\frac{|C|^2 V_{pq}V_{rs}}{i\omega_{rs}+t_0^{-1}}(1-e^{-(i\omega_{rs}+t_0^{-1})t}) , \quad (5.6)$$

whose real and imaginary parts show a damped oscillatory behavior which becomes smoother as t_0 becomes smaller (constant for $t_0=0$). The functions $\hat{K}_{jk,lm}(t)$, being sums of terms of this type, have a similar behavior. Even though the bath correlation functions do not generally have the simple form of Eq. (4.6), we assume that the matrix elements $\hat{K}_{jk,lm}(t)$ continue to show a similar temporal behavior, that is, the smaller the typical bath correlation time t_c, the smoother it becomes.

As in the previous cases, due to the presence of the mixing terms $\hat{K}_{jk,lm}(t)\sigma_{lm}(t)$ with $(l,m)\neq(j,k)$, the evolution of coherences and populations are not generally independent. Except in very simple cases, the problem should be studied in the framework of the secular approximation.

A. The secular approximation

In the Markovian limit, the matrix elements $\hat{K}_{jk,lm}(t)$ become constant and equal to $\hat{K}_{jk,lm}(\infty)=\hat{R}_{jk,lm}$ [Eq. (5.5)]. Therefore, if the relaxation of S is not too far from the Markovian limit, as can be expected within a weak-coupling theory, the spectral representation of the terms $\hat{K}_{jk,lm}(t)\sigma_{lm}(t)$ in Eq. (5.1) is not going to differ very much from the corresponding representation of the Markovian limit. Then, the sufficient conditions (3.7) for the application of the secular approximation will continue to be valid if $\hat{R}_{jk,lm}$ is substituted by $\hat{K}_{jk,lm}(\infty)$, calculated from Eq. (5.2).

The application of the Laplace-Fourier transformation to Eq. (5.1) does not offer any advantage, and therefore, in this case, it is more useful to carry out a study in the domain of times. For a system with a nonequidistant energy spectrum, retaining only the secular terms in Eq. (5.1) and separating the evolution equations for coherences and populations, we have

$$\dot{\sigma}_{jk}(t)=-[i\omega_{jk}+\hat{K}_{jk,jk}(t)]\sigma_{jk}(t) , \quad (5.7)$$

$$\dot{\sigma}_{jj}(t)=-\hat{K}_{jj,jj}(t)\sigma_{jj}(t)-\sum_{k\,(\neq j)}\hat{K}_{jj,kk}(t)\sigma_{kk}(t) . \quad (5.8)$$

A more general set of equations than these have been found by Mukamel[37] for molecular multiphoton processes.

While Eq. (5.8) for the population relaxation does not allow us to go any further without a specific model, the integration of Eq. (5.7) leads to the following expression for the loss of phase:

$$\sigma_{jk}(t)=\sigma_{jk}(0)e^{-i\omega_{jk}t}e^{-\Omega_{jk}(t)} , \quad (5.9)$$

where

$$\Omega_{jk}(t)=\int_0^t dt_1\hat{K}_{jk,jk}(t_1) = \int_0^t d\tau(t-\tau)e^{i\omega_{jk}\tau}\hat{W}_{jk,jk}(\tau) . \quad (5.10)$$

For times such that $t\ll t_c$, the functions $\Omega_{jk}(t)$ [Eq. (5.10)] show a quadratic behavior in t:

$$\Omega_{jk}(t)\simeq\tfrac{1}{2}\hat{W}_{jk,jk}(0)t^2 \quad (5.11)$$

and Eq. (5.9) may be written as

$$\sigma_{jk}(t)=\sigma_{jk}(0)e^{-i\omega_{jk}t}e^{-\hat{W}_{jk,jk}(0)t^2/2} . \quad (5.12)$$

This equation gives the time evolution of the coherences in the limit of short times and, therefore, determines the PTOC behavior in the "wings" of $\bar{\sigma}_{jk}(\omega)$, which does not coincide with that prescribed by Eq. (4.13) for the TTOC scheme.

For times such that $t\gg t_c$, the functions $\Omega_{jk}(t)$ of Eq. (5.10) show a linear behavior with t,

$$\Omega_{jk}(t)\simeq t\int_0^\infty d\tau\, e^{i\omega_{jk}\tau}\hat{W}_{jk,jk}(\tau) = \bar{\hat{W}}_{jk,jk}(\omega_{jk})t , \quad (5.13)$$

and, taking into account Eq. (3.3), Eq. (5.9) becomes Eq. (3.11), valid in the Markovian limit (this limit is sometimes known as the large time limit).

The deviation $\sigma_{jk}(t)$ with respect to the Markovian behavior may be treated as a perturbation in the interaction S-B. The factor $\exp[-\Omega_{jk}(t)]$ in Eq. (5.9) has the form

$$\exp\left[-\lambda^2\int_0^t d\tau(t-\tau)f(\tau)\right]$$

[Eq. (5.10)], λ being a parameter that characterizes the intensity of the interaction. Using the expansion

$$\exp\left[-\lambda^2\int_0^t d\tau(t-\tau)f(\tau)\right]=\exp\left[-t\lambda^2\int_0^\infty d\tau f(\tau)\right]\left[1+\lambda^2\left[t\int_0^\infty d\tau f(\tau)-\int_0^t d\tau(t-\tau)f(\tau)\right]+\mathcal{O}(\lambda^4)\right] \quad (5.14)$$

and taking into account Eqs. (3.3a) and (3.9)

$$\int_0^\infty d\tau\, e^{i\omega_{jk}\tau}\hat{W}_{jk,jk}(\tau)=\hat{R}_{jk,jk}=\Gamma_{jk}+i\Delta_{jk} , \quad (5.15)$$

we obtain from Eq. (5.9)

$$\sigma_{jk}(t)=\sigma_{jk}(0)e^{-i\tilde{\omega}_{jk}t}e^{-\Gamma_{jk}t}[1+t(\Gamma_{jk}+i\Delta_{jk})-\Omega_{jk}(t)] , \quad (5.16)$$

which gives the deviation with respect to the Markovian behavior [Eq. (3.11)] up to the second order in the interaction within the PTOC scheme.

B. Mixing between coherences

In the PTOC evolution, the analysis of interferences between coherences and populations presents similar problems to those of the TTOC evolution. In particular, if the interferences between the time evolution of a certain set of coherences is small and these coherences are independent of the other matrix elements of $\sigma(t)$, an iterative method may be used. In this method Eq. (5.9) is taken as a zeroth-order solution. The substitution of Eq. (5.9) in Eq. (5.1) yields

$$\dot{\sigma}_{jk}(t)=-[i\omega_{jk}+\hat{K}_{jk,jk}(t)]\sigma_{jk}(t)-\sum_{l,m}\sigma_{lm}(0)\hat{K}_{jk,lm}(t)e^{-i\omega_{lm}t}e^{-\Omega_{lm}t}\ ,\quad (l,m)\neq(j,k) \tag{5.17}$$

which has the formal solution

$$\sigma_{jk}(t)=e^{-i\omega_{jk}t}e^{-\Omega_{jk}t}\left[\sigma_{jk}(0)-\sum_{l,m}\sigma_{lm}(0)\int_0^t d\tau\,\hat{K}_{jk,lm}(\tau)e^{-i(\omega_{lm}-\omega_{jk})\tau}e^{-[\Omega_{lm}(\tau)-\Omega_{jk}(\tau)]}\right]\ ,\quad (l,m)\neq(j,k)\ . \tag{5.18}$$

In this equation, as in Eq. (4.14), the terms which most contribute to the sum will be those for which the indices (l,m) correspond to the frequencies ω_{lm} close to ω_{jk}.

VI. SUMMARY

In this paper we have analyzed the quantum relaxation of a small system weakly coupled to a bath, within the TTOC and PTOC non-Markovian schemes, which coincide in the Markovian limit. This analysis was carried out by the study, in each case, of the corresponding time-evolution equations of the matrix elements of the reduced-density matrix $\sigma(t)$ of the system, in the representation of the eigenstates of its free Hamiltonian (for simplicity, we assume that its spectrum is nondegenerate). The integration of these equations is not a trivial task, because the evolutions of the matrix elements of $\sigma(t)$ are intercoupled by the corresponding relaxation superoperators. The problem is simplified when it is possible to apply the secular approximation, which allows the uncoupling of the populations from the coherences, the latter continuing to be interconnected only when they correspond to equal frequencies (e.g., in the case of an equidistant energy spectrum). We stress the importance that the form of the energy spectrum of the system may have in the solution of the problem. In particular, in the case of a nonequidistant energy spectrum the secular solution for the coherences is very simple because they evolve independently of each other. The TTOC and PTOC solutions are, therefore, given by Eqs. (4.10) and (5.9), respectively, which coincide in the Markovian limit in which each coherence decays exponentially in time. When the mixing between coherences is small, an iterative method is developed. This method leads in the TTOC and PTOC schemes to the solutions (4.14) and (5.18), respectively, up to second order in the interaction system bath.

We connect the matrix elements of the corresponding relaxation superoperators with the bath correlation functions in Eqs. (3.3), (4.4), and (5.2). These equations are the basis for the application of these formalisms to a particular problem in which a specific model for the bath is adopted. In a subsequent paper,[24] we shall apply the results obtained to the calculation of spectral line shapes.

APPENDIX: EVALUATION OF THE MATRIX ELEMENTS $\hat{W}_{jk,lm}(t)$

Taking into account that $\mathscr{L}_S$ is, in the $\{\,|j\alpha,k\beta)\}$ basis of the total Liouville space, a diagonal superoperator which depends only on system S, we have from Eq. (2.13):

$$\hat{W}_{jk,lm}(t)=\langle\mathscr{L}'(t)e^{-i\mathscr{L}_s t}\mathscr{L}'\rangle_{jk,lm}=\sum_{\alpha,\beta}\rho_B^0(\beta)\sum_{p,q}\sum_{\nu,\epsilon}\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}(t)\mathscr{L}'_{p\nu,q\epsilon,l\beta,m\beta}e^{-i\omega_{pq}t}\ , \tag{A1}$$

where j, k, l, m, p, and q are states of system S and α, β, ν, and ϵ are bath states. Because $\mathscr{L}_B$ is, in the basis $\{\,|j\alpha,k\beta)\}$, a superoperator belonging exclusively to the bath, Eq. (2.13b) yields

$$\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}(t)=(e^{i\mathscr{L}_B T}\mathscr{L}'e^{-i\mathscr{L}_B t})_{j\alpha,k\alpha,p\nu,q\epsilon}=\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}e^{-i\omega_{\nu\epsilon}t}\ , \tag{A2}$$

with

$$\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}\equiv\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}(0)\ .$$

Substituting (A2) in (A1) and reordering factors, we obtain

$$\hat{W}_{jk,lm}(t)=\sum_{p,q}e^{-i\omega_{pq}t}\sum_{\alpha,\beta}\rho_B^0(\beta)\sum_{\nu,\epsilon}e^{-i\omega_{\nu\epsilon}t}\mathscr{L}'_{j\alpha,k\alpha,p\nu,q\epsilon}\mathscr{L}'_{p\nu,q\epsilon,l\beta,m\beta}\ . \tag{A3}$$

Making use now of Eq. (2.6b) for the matrix elements of $\mathscr{L}'$, we obtain

$$\mathscr{L}'_{j\alpha,k\alpha,pv,q\epsilon}\mathscr{L}'_{pv,q\epsilon,l\beta,m\beta}=\hbar^{-2}(H'_{j\alpha,pv}H'_{pv,l\beta}\delta_{kq}\delta_{qm}\delta_{\alpha\epsilon}\delta_{\epsilon\beta}$$
$$-H'_{j\alpha,pv}H'_{m\beta,q\epsilon}\delta_{kq}\delta_{pl}\delta_{\alpha\epsilon}\delta_{v\beta}-H'_{q\epsilon,k\alpha}H'_{pv,l\beta}\delta_{jp}\delta_{qm}\delta_{\alpha v}\delta_{\epsilon\beta}$$
$$+H'_{q\epsilon,k\alpha}H'_{m\beta,q\epsilon}\delta_{jp}\delta_{pl}\delta_{\alpha v}\delta_{v\beta})\ . \tag{A4}$$

The substitution of Eq. (A4) into Eq. (A3) yields

$$\hat{W}_{jk,lm}(t)=\hbar^{-2}\sum_{p,q}e^{-i\omega_{pq}t}\left[\delta_{kq}\delta_{qm}\sum_{\alpha,v}\rho_B^0(\alpha)e^{-i\omega_{v\alpha}t}H'_{j\alpha,pv}H'_{pv,l\alpha}-\delta_{kq}\delta_{pl}\sum_{\alpha,\beta}\rho_B^0(\beta)e^{-i\omega_{\beta\alpha}t}H'_{j\alpha,p\beta}H'_{m\beta,q\alpha}\right.$$
$$\left.-\delta_{jp}\delta_{qm}\sum_{\alpha,\beta}\rho_B^0(\beta)e^{-i\omega_{\alpha\beta}t}H'_{q\beta,k\alpha}H'_{\beta\alpha,l\beta}+\delta_{jp}\delta_{pl}\sum_{\alpha,\epsilon}\rho_B^0(\alpha)e^{-i\omega_{\alpha\epsilon}t}H'_{q\epsilon,k\alpha}H'_{m\alpha,q\epsilon}\right]\ . \tag{A5}$$

Defining the time correlation function for two bath operators A and B as

$$\langle A(t)B\rangle=\sum_{\alpha,\alpha'}\rho_B^0(\alpha)e^{i\omega_{\alpha\alpha'}t}A_{\alpha\alpha'}B_{\alpha'\alpha}=\langle AB(-t)\rangle\ , \tag{A6}$$

Eq. (A5) may be written in the form of

$$\hat{W}_{jk,lm}(t)=\hbar^{-2}\left[\delta_{km}\sum_{p}e^{-i\omega_{pk}t}\langle H'_{jp}(t)H'_{pl}\rangle+\delta_{jl}\sum_{q}e^{-i\omega_{jq}t}\langle H'_{mq}H'_{qk}(t)\rangle\right.$$
$$\left.-e^{-i\omega_{jm}t}\langle H'_{mk}(t)H'_{jl}\rangle-e^{-i\omega_{lk}t}\langle H'_{mk}\,H'_{jl}(t)\rangle\right]\ , \tag{A7}$$

which is the expression we were looking for. Taking into account the relationship[38]

$$\langle A(t)B\rangle^*=\langle B^\dagger A^\dagger(t)\rangle$$

and the Hermeticity of H', expression (A7) may also be written in the form

$$\hat{W}_{jk,lm}(t)=\hbar^{-2}\left[\delta_{km}\sum_{p}e^{-i\omega_{pk}t}\langle H'_{jp}(t)H'_{pl}\rangle+\delta_{jl}\sum_{q}e^{-i\omega_{jq}t}\langle H'_{kq}(t)H'_{qm}\rangle^*\right.$$
$$\left.-e^{-i\omega_{jm}t}\langle H'_{mk}(t)H'_{jl}\rangle-e^{-i\omega_{lk}t}\langle H'_{lj}(t)\,H_{km}\rangle^*\right]\ . \tag{A8}$$

Some matrix elements of $\hat{W}(t)$ of particular interest are

$$\hat{W}_{jk,jk}(t)=\hbar^{-2}\left[\sum_{p\,(\neq j)}e^{-i\omega_{pk}t}\langle H'_{jp}(t)H'_{pj}\rangle+\sum_{q\neq k}e^{-i\omega_{jq}t}\langle H'_{kq}H'_{qk(t)}\rangle\right.$$
$$\left.+e^{-i\omega_{jk}t}[\langle H'_{jj}(t)H'_{jj}\rangle+\langle H'_{kk}H'_{kk}(t)\rangle-\langle H'_{kk}(t)H'_{jj}\rangle-\langle H'_{kk}\,H'_{jj}(t)\rangle]\right]\ ,\quad j\neq k \tag{A9a}$$

$$\hat{W}_{jj,jj}(t)=\hbar^{-2}\left[\sum_{p\,(\neq j)}e^{-i\omega_{pj}t}\langle H'_{jp}(t)H'_{pj}\rangle+\text{c.c.}\right]\ , \tag{A9b}$$

$$\hat{W}_{jj,kk}(t)=-\hbar^{-2}[e^{-i\omega_{jk}t}\langle H'_{kj}(t)H'_{jk}\rangle+\text{c.c.}]\ ,\quad j\neq k\ . \tag{A9c}$$

We also have the relationship

$$\hat{W}_{jj,jj}(t)=-\sum_{k\,(\neq j)}\hat{W}_{kk,jj}(t)\ . \tag{A10}$$

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