

## Relaxation of quantum systems weakly coupled to a bath. II. Formal analysis of the total-time-ordering-cumulant and partial-time-ordering-cumulant spectral line shapes

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Given a quantum system of a few degrees of freedom in weak interaction with a bath, the expressions which connect its total-time-ordering-cumulant and partial-time-ordering-cumulant relaxation with the corresponding spectral line shapes of dipolar absorption are deduced. For simplicity we consider a system with a nondegenerate and nonequidistant energy spectrum. A special study in the cases of isolated resonances and of a weak interference effect between resonances is made.

### I. INTRODUCTION

There is a great variety of experimental methods for the investigation of intra- or intermolecular motions, which, although based on physical phenomena of very different natures, deal with the problem using a general scheme consisting of analyzing the response of a sample to a small disturbance, controlled from the outside.<sup>1</sup> The information supplied by this kind of "probe experiment" is often related to the time-correlation functions of certain observables of the system evaluated in the absence of the disturbance; hence the interest in carrying out in each case the connection between the corresponding correlation functions and the molecular motion.

In paper I (Ref. 2) we studied the total-time-ordering-cumulant (TTOC) and partial-time-ordering-cumulants (PTOC) master equations for the relaxation of a quantum system  $S$  of few degrees of freedom in weak interaction with a thermal bath  $B$ . Both equations were obtained without making use of the Markovian limit hypothesis<sup>3</sup> (in this limit the TTOC and PTOC equations coincide). Let us now suppose, furthermore, that  $S$  has a certain dipolar moment. Then, within the general context of probe experiments we shall study the corresponding spectral line shapes when the  $S$  relaxation is governed either by the Markovian, the TTOC, or the PTOC equations. The formalism is applicable to the study of a great variety of problems such as the vibration spectra or the rotation spectra of impurity molecules in condensed media.

### II. CONNECTION BETWEEN THE SPECTRAL LINE SHAPE AND THE REDUCED-DENSITY MATRIX

In the framework of the linear-response theory, the spectral line shape can be written as<sup>4,5</sup>

$$I(\omega) \propto \text{Re} \left[ \int_0^\infty dt e^{i\omega t} \text{Tr}[\mu(t)\mu(0)\rho(0)] \right]. \quad (2.1)$$

The dipole moment operator  $\mu(0)$  of the system  $S$  possesses only off-diagonal matrix elements in the  $\{|j\rangle\}$  basis<sup>6</sup> and, hence, can be written as

$$\mu = \sum_{j,k} \mu_{jk} |j\rangle\langle k| + \text{H.c.}, \quad j > k. \quad (2.2)$$

According to the linear-response theory,  $\rho(0)$  in Eq. (2.1) is the equilibrium density matrix of the complete system  $S \oplus B$  in the absence of the external disturbance. If the only information available on the complete system is its temperature  $T$ , we may consider for  $\rho(0)$  a canonical distribution which is diagonal in the  $\{|j\alpha\rangle\}$  basis:

$$\rho_{j\alpha, k\beta}(0) = \sigma_j^0 \rho_B^0(\alpha) \delta_{jk} \delta_{\alpha\beta}, \quad (2.3)$$

with

$$\sigma_j^0 = \frac{\exp(-E_j/k_B T)}{\sum_j \exp(-E_j/k_B T)}, \quad \rho_B^0 = \frac{\exp(-E_\alpha/k_B T)}{\sum_\alpha \exp(-E_\alpha/k_B T)}. \quad (2.4)$$

Using the fact that the density matrix  $\sigma^0$  depends only on the system  $S$  coordinates, and hence is not affected by the trace over the bath, we obtain from Eq. (2.1), for the absorption line shape,

$$I(\alpha) \propto \sum_{\substack{j,k \\ k>j}} \sigma_j^0 \mu_{kj}(0) \text{Re} \left[ \int_0^\infty dt e^{i\omega t} \langle \mu_{jk}(t) \rangle \right], \quad (2.5)$$

where

$$\begin{aligned} \langle \mu_{jk}(t) \rangle &= \text{Tr}_B [\mu_{jk}(t) \rho_B^0] \\ &= \sum_\alpha \rho_B^0(\alpha) \langle j\alpha | \mu(t) | k\alpha \rangle. \end{aligned} \quad (2.6)$$

From the Heisenberg equation and making use of the interaction representation and of the Liouville formalism, one obtains

$$\mu(t) = \hat{A}^\dagger(t) e^{i\mathcal{L}S t} \mu(0), \quad (2.7)$$

where the superoperator  $\hat{A}^\dagger(t)$  is the Hermitian conjugate of  $\hat{A}(t)$  defined by Eq. (A1) of the Appendix. Taking in Eq. (2.7) the matrix elements in the representation of eigenstates of  $H_S$  and averaging over the bath, we have

$$\begin{aligned} \langle \mu_{jk}(t) \rangle &= \sum_{\substack{l,m \\ l \neq m}} \sum_{\alpha, \beta} \rho_B^0(\alpha) \hat{A}_{j\alpha, k\alpha; l\beta, m\beta}^\dagger(t) e^{i\omega_{lm}t} \mu_{lm}(0) \\ &= \sum_{\substack{l,m \\ l \neq m}} \sum_{\alpha, \beta} \rho_B^0(\alpha) \hat{A}_{m\beta, l\beta; k\alpha, j\alpha}(t) e^{i\omega_{lm}t} \mu_{lm}(0) \end{aligned} \quad (2.8)$$

in which we make use of the relationship (A8).

Equation (2.8) can be written as

$$I(\omega) \propto \sum_{\substack{j,k \\ k > j}} \sigma_j^0 \mu_{kj}(0) \sum_{\substack{l,m \\ l \neq m}} \mu_{lm}(0) \text{Re} \left[ \int_0^\infty dt e^{i\omega t} \sigma_{ml}^{(kj)}(t) \right] = \sum_{\substack{j,k \\ k > j}} \sigma_j^0 \mu_{kj}(0) \sum_{\substack{l,m \\ l \neq m}} \mu_{lm}(0) \text{Re}[\bar{\sigma}_{ml}^{(kj)}(\omega)] . \quad (2.11)$$

On the other hand, taking matrix elements in the reduced-density matrix operator [Eq. (2.10) of paper I], we have

$$\begin{aligned} \sigma_{ml}(t) &= e^{-i\omega_{ml}t} \sum_{p,q} \langle \hat{A}(t) \rangle_{ml,pq} \sigma_{pq}(0) \\ &= e^{-i\omega_{ml}t} \sum_{p,q} \sum_{\alpha, \beta} \rho_B^0(\alpha) \hat{A}_{m\beta, l\beta; p\alpha, q\alpha}(t) \sigma_{pq}(0) . \end{aligned} \quad (2.12)$$

If we arbitrarily impose on this equation the condition

$$\sigma_{pq}(0) = \delta_{pk} \delta_{qj} \quad \forall (p, q) \quad (2.13)$$

Eqs. (2.12) and (2.10) coincide, and the conditional probability  $\sigma_{ml}^{(kj)}(t)$  can be found from the formulas obtained in paper I for the evolution of the nondiagonal matrix elements of the reduced-density operator  $\sigma(t)$ . This fact allows us to formally link two problems: the  $S$  relaxation in  $B$  and the spectral line shape.

### III. THE MARKOVIAN SPECTRAL LINE SHAPE

Let us assume that the  $S$ - $B$  interaction is sufficiently weak for applying the secular approximation.<sup>2</sup> From Eq. (3.10) of paper I and with the conditions (2.13) we have

$$\bar{\sigma}_{mk}^{(kj)}(\omega) = \frac{i\delta_{mk}\delta_{lj}}{\omega - \tilde{\omega}_{ml} + i\Gamma_{ml}} , \quad (3.1)$$

where  $\omega_{ml}$  and  $\Gamma_{ml}$  are given by Eqs. (3.9) of paper I.

The substitution of Eq. (3.1) in expression (2.11) allows us to obtain

$$I_0^M(\omega) \propto \sum_{\substack{j,k \\ k > j}} \sigma_j(0) |\mu_{kj}(0)|^2 \frac{\Gamma_{kj}}{(\omega - \tilde{\omega}_{kj})^2 + \Gamma_{kj}^2} , \quad (3.2)$$

i.e., in the Markovian limit and in the secular approximation, the absorption line shape consists of a sum of Lorentzian resonances (or lines) located around the frequencies  $\tilde{\omega}_{kj}$  and with a linewidth  $\Gamma_{kj}$ . Since the intensity of each sum depends on the population  $\sigma_j^0$  of the level  $|j\rangle$  [Eq. (2.4)], the aspect of the spectral line shape depends considerably on the temperature.

We see, then, that conditions (3.7) in paper I, which guarantee the secular approximation, are sufficient for a Lorentzian profile  $I_0^M(\omega)$ . Therefore, when the linewidths of the neighboring resonances are smaller than their spac-

$$\langle \mu_{jk}(t) \rangle = \sum_{\substack{l,m \\ l \neq m}} \sigma_{ml}^{(kj)}(t) \mu_{lm}(0) . \quad (2.9)$$

Here  $\sigma_{ml}^{(kj)}(t)$  plays the role of a conditional probability for  $\mu_{jk}(t)$  and is given by

$$\sigma_{ml}^{(kj)}(t) = e^{-i\omega_{ml}t} \sum_{\alpha, \beta} \rho_B^0(\alpha) \hat{A}_{m\beta, l\beta; k\alpha, j\alpha}(t) . \quad (2.10)$$

The absorption line shape (2.5) can now be written as

ing, i.e., when the lines are isolated, the secular approximation is guaranteed. If there is overlapping between resonances, the nonsecular terms  $\hat{R}_{lm,pq} \bar{\sigma}_{pq}(\omega)$ , with  $(l, m) \neq (p, q)$  in Eq. (3.6) of paper I, may be non-negligible (except when the coupling coefficients  $\hat{R}_{lm,pq}$  are zero) and the well-known interference line effect shows up. We shall deal with this problem in Secs. IV and V for the cases of the TTOC and PTOC line shapes, respectively. The results obtained in those sections are easily transferable to the more particular situation of the Markovian limit.

## IV. THE TTOC SPECTRAL LINE SHAPE

### A. Isolated resonances

If the lines of the profile are sufficiently isolated we can use Eq. (4.10) of paper I, which corresponds to the application of the secular approximation in the TTOC scheme. With the conditions (2.13), we obtain for the spectral functions of  $\sigma_{ml}^{(kj)}(t)$

$$\bar{\sigma}_{ml}^{(kj)}(\omega) = \frac{i\delta_{mk}\delta_{jl}}{\omega - \omega_{ml} + i\tilde{W}_{ml,ml}(\omega)} \quad (4.1)$$

which, substituted into Eq. (2.11), leads to the following absorption profile:

$$I_0^T(\omega) \propto - \sum_{\substack{j,k \\ k > j}} \sigma_j^0 |\mu_{kj}(0)|^2 \text{Im}[\Lambda_{kj}(\omega)] , \quad (4.2a)$$

$$\Lambda_{kj}(\omega) = \frac{1}{\omega - \omega_{kj} + i\tilde{W}_{kj,kj}(\omega)} . \quad (4.2b)$$

When the secular approximation is justified, Eqs. (4.2) give the TTOC absorption line shape as a sum of resonances around the frequencies  $\omega_{kj}$ .

From a quantitative point of view, the behavior of  $\text{Im}[\Lambda_{kj}(\omega)]$  can be analyzed for some ranges of the  $\omega$  values without specifying a particular expression for the bath correlation functions (3.6), and therefore, for the matrix elements  $\tilde{W}_{kj,kj}(\omega)$ . In particular, for  $\omega$  such that  $|\omega - \omega_{kj}| \ll t_c^{-1}$  (where  $t_c$  is the bath correlation time), the function  $\tilde{W}_{kj,kj}(\omega)$  remains practically constant and equal to  $\tilde{W}_{kj,kj}(\omega_{kj})$  (Ref. 2). Then Eq. (4.2b) gives

$$\Lambda_{kj}(\omega) \simeq \frac{1}{\omega - \tilde{\omega}_{kj} + i\Gamma_{kj}} \quad (4.3)$$

and each resonance becomes proportional to

$$\text{Im}[\Lambda_{kj}(\omega)] \simeq -\frac{\Gamma_{kj}}{(\omega - \tilde{\omega}_{kj})^2 + \Gamma_{kj}^2}, \quad |\omega - \omega_{kj}| \ll t_c^{-1}. \quad (4.4)$$

On the contrary, far out in the wings of a resonance, the dependence of  $\widehat{W}_{kj,kj}(\omega)$  on  $\omega$  is important. In this region  $|\widehat{W}_{kj,kj}(\omega)| \ll |\omega - \omega_{kj}|$  and, hence, in Eq. (4.2b) a series expansion in powers of  $\widehat{W}(\omega)$  may be carried out, giving

$$\Lambda_{kj}(\omega) \simeq \frac{1}{\omega - \omega_{kj}} \left| 1 + \frac{i\widehat{W}_{kj,kj}(\omega)}{\omega - \omega_{kj}} \right| \quad (4.5)$$

and

$$\text{Im}[\Lambda_{kj}(\omega)] \simeq \frac{\text{Re}[\widehat{W}_{kj,kj}(\omega)]}{(\omega - \omega_{kj})^2}, \quad |\omega - \omega_{kj}| \gg |\widehat{W}_{kj,kj}(\omega)| \quad (4.6)$$

retaining only up to the first-order term.

Between the Lorentzian behavior (4.4) around its maximum and the behavior (4.6) in the wings, the shape of a resonance depends on the function  $\widehat{W}_{kj,kj}(\omega)$ , which produces an asymmetry in the resonance. The dependence of  $\widehat{W}_{kj,kj}(\omega)$  on  $\omega$  will be smoother the more the relaxation of  $S$  approaches the Markovian limit where the function is constant.

## B. Interference between resonances

Consider now a certain overlapping between resonances and that the coupling coefficients  $\widehat{W}_{ml,pq}(\omega)$ , with  $(m,l) \neq (p,q)$ , are not zero. Thus an interference effect between resonances appears and the profile (4.2b) is no longer valid. It is said, then, that the profile is nonadditive, in the sense that it is not the sum of secular terms associated with the various resonances. If this interference effect is weak enough to allow the use of the iterative method developed in Sec. IV of paper I, the TTOC line shape can be easily obtained; Eq. (4.14) of paper I, with the conditions (2.13), yields (up to the first order in the iteration)

$$\bar{\sigma}_{ml}^{(kj)}(\omega) = \frac{1}{\omega - \omega_{ml} + i\widehat{W}_{ml,ml}(\omega)} \left[ i\delta_{mk}\delta_{lj} + \frac{\widehat{W}_{ml,kj}(\omega)}{\omega - \omega_{kj} + i\widehat{W}_{kj,kj}(\omega)} (1 - \delta_{mk}\delta_{lj}) \right], \quad (4.7)$$

which, substituted into Eq. (2.11), leads to the following TTOC absorption profile:

$$I^T(\omega) = I_0^T(\omega) + I_1^T(\omega), \quad (4.8)$$

where  $I_0^T(\omega)$  is given by Eq. (4.2), and

$$I_1^T(\omega) \propto \sum_{\substack{j,k \\ k>j}} \sigma_j^0 \mu_{kj}(0) \sum_{\substack{l,m \\ l \neq m \\ (l,m) \neq (j,k)}} \mu_{lm}(0) \text{Re}[\widehat{W}_{ml,kj}(\omega) \Lambda_{kj}(\omega) \Lambda_{ml}(\omega)] \quad (4.9)$$

is the TTOC correcting profile, up to second order with respect to the  $S$ - $B$  interaction, due to the interference effect between resonances.

Following Eq. (4.2b), the values of the functions  $\Lambda_{kj}(\omega)$  and  $\Lambda_{ml}(\omega)$  of Eq. (4.9) become significant only in a certain range of the  $\omega$  values around the frequencies  $\omega_{kj}$  and  $\omega_{ml}$ , respectively. Therefore, no negligible overlapping can exist only for indices  $(m,l)$  corresponding to frequencies  $\omega_{ml}$  close to  $\omega_{kj}$  [note that for Eq. (4.9) to be applicable, a weak overlapping between these functions is necessary]. In Eq. (4.9) the importance of the contribution of each term to the correcting profile will also depend on the coupling functions  $\widehat{W}_{ml,kj}(\omega)$  and on the remaining coefficients and, in particular, on the temperature  $T$  through the factor  $\sigma_j^0$ .

## V. THE PTOC SPECTRAL LINE SHAPE

### A. Isolated resonances

From Eq. (5.9) of paper I, with the conditions (2.13), we have for the time evolution  $\sigma_{ml}^{(kj)}(t)$

$$\sigma_{ml}^{(kj)}(t) = \delta_{mk}\delta_{lj} e^{-i\omega_{ml}t} \exp \left[ -\int_0^t dt_1 \widehat{K}_{ml,ml}(t_1) \right] \quad (5.1)$$

which, when substituted into Eq. (2.11), yields for the PTOC absorption line shape in the secular approximation

$$I_0^P(\omega) \propto \sum_{\substack{j,k \\ k>j}} \sigma_j(0) |\mu_{kj}(0)|^2 \times \text{Re} \left[ \int_0^\infty dt e^{i(\omega - \omega_{kj})t} e^{-\Omega_{kj}(t)} \right] \quad (5.2a)$$

with

$$\begin{aligned} \Omega_{kj}(t) &= \int_0^t dt_1 \widehat{R}_{kj,kj}(t_1) \\ &= \int_0^t d\tau (t - \tau) e^{i\omega_{kj}\tau} \widehat{W}_{kj,kj}(\tau). \end{aligned} \quad (5.2b)$$

Once the temperature has been fixed, the actual form of the spectral line shape  $I_0^P(\omega)$  will depend on the temporal behavior of the function  $\Omega_{kj}(t)$ , which should be determined considering specific models. If the time evolution of the system  $S$  is not far from the Markovian limit, expansion (5.14) and Eq. (2.17) of paper I give, up to the second order in the  $S$ - $B$  interaction,

$$e^{-\Omega_{kj}t} = e^{-t\hat{R}_{kj,kj}} [1 + t\hat{R}_{kj,kj} - \Omega_{kj}(t)] \quad (5.3)$$

which, substituted into Eq. (5.2a), yields for the PTOC profile

$$I_0^D(\omega) = \sum_{\substack{j,k \\ k>j}} \sigma_j^0 |\mu_{kj}(0)|^2 \text{Re} \left[ \frac{\widehat{W}_{kj,kj}(\omega - \Delta_{kj} + i\Gamma_{kj}) - \widehat{W}_{kj,kj}(\omega_{kj})}{[(\omega - \tilde{\omega}_{kj}) + i\Gamma_{kj}]^2} \right] \quad (5.5)$$

gives, up to the second order, the deviation with respect to the Markovian behavior.

### B. Interferences between resonances

In the case of a small overlapping between resonances, an iterative method may be developed as in the TTOC case. Equation (5.18) in paper I, with the conditions (2.13), yields

$$\sigma_{ml}^{(kj)}(t) = e^{-i\omega_{ml}t} e^{-\Omega_{ml}(t)} \left[ \delta_{mk} \delta_{lj} - (1 - \delta_{mk} \delta_{lj}) \int_0^t d\tau \hat{K}_{ml,kj}(\tau) e^{-i(\omega_{kj} - \omega_{ml})\tau} e^{-[\Omega_{kj}(\tau) - \Omega_{ml}(\tau)]} \right]. \quad (5.6)$$

The substitution of (5.8) into expression (2.11) leads to the following PTOC absorption profile:

$$I^P(\omega) = I_0^P(\omega) + I_1^P(\omega), \quad (5.7)$$

where  $I_0^P(\omega)$  is given by Eq. (5.2) and

$$I_1^P(\omega) \propto - \sum_{\substack{j,k \\ k>j}} \sigma_j^0 \mu_{kj}(0) \sum_{\substack{l,m \\ l \neq m \\ (l,m) \neq (j,k)}} \mu_{ml}(0) \text{Re}[\Phi(\omega)], \quad (5.8a)$$

where

$$\begin{aligned} \{\Phi(\omega)\} &= \int_0^\infty dt e^{i(\omega - \omega_{ml})t} e^{-\Omega_{ml}(t)} \\ &\times \int_0^t d\tau \hat{K}_{ml,kj}(\tau) e^{-i(\omega_{kj} - \omega_{ml})\tau} \\ &\times e^{-[\Omega_{kj}(\tau) - \Omega_{ml}(\tau)]}. \end{aligned} \quad (5.8b)$$

## VI. TWO CASES

### A. Diagonal interaction and exponential correlation

With this very simple example we emphasize, more positively than in Eqs. (4.2) and (5.2), how the TTOC and PTOC schemes lead to different spectral line shapes, except in the Markovian limit in which they coincide. Let us assume that  $H'$  is factorized in the form

$$H' = \hat{\kappa} V F, \quad (6.1)$$

where  $V$  and  $F$  are, respectively,  $S$  and  $B$  operators. Let us also assume that  $V$  is diagonal in the representation of the  $H_S$  eigenstates and that the autocorrelation function of  $F$  is exponential with a decay time  $t_c$ . We then have

$$\begin{aligned} \langle H'_{ab}(t) H'_{cd} \rangle &= \hat{\kappa}^2 V_{ab} V_{cd} \langle F(t) F \rangle \\ &= \hat{\kappa}^2 |c|^2 V_{aa} V_{cc} e^{-|t|/t_c} \delta_{ab} \delta_{cd}, \end{aligned} \quad (6.2)$$

where  $|c|^2$  is a parameter which characterizes the contribution of the bath operator  $F$  to the intensity of the  $S$ - $B$  interaction. The substitution of Eq. (6.2) into Eq. (5.2) of paper I yields for the matrix elements of the superoperator  $\hat{W}(t)$

$$I_0^P(\omega) = I_0^M(\omega) + I_0^D(\omega), \quad (5.4)$$

where  $I_0^M(\omega)$  is the Markovian profile given by Eq. (3.2), and

$$\widehat{W}_{ml,kj}(t) = |c|^2 (V_{kk} - V_{jj})^2 e^{-i\omega_{kj}t} e^{-t/t_c} \delta_{mk} \delta_{lj}. \quad (6.3)$$

Taking the Fourier-Laplace transformation, we have

$$\widehat{W}_{ml,kj}(\omega) = - \frac{|c|^2 (V_{kk} - V_{jj})^2}{i(\omega - \omega_{kj}) - t_c^{-1}} \delta_{mk} \delta_{lj}. \quad (6.4)$$

According to this expression, the coupling coefficients  $\widehat{W}_{ml,kj}(\omega)$ , with  $(m, l) \neq (k, j)$ , are zero. Therefore, in this case of diagonal interaction, there are no interference effects, i.e., the resonances are additive even if they do not overlap.

If the relaxation of  $S$  takes place following the TTOC scheme, the substitution of Eq. (6.4) into Eq. (4.6) gives, for the corresponding spectral profile,

$$\begin{aligned} I^T(\omega) &\propto \sum_{\substack{j,k \\ k>j}} \sigma_j^0 |\mu_{kj}(0)|^2 \\ &\times \frac{\overline{W}'_{kj}(\omega)}{[\omega - \omega_{kj} - \overline{W}''_{kj}(\omega)] + W_{kj}(\omega)}, \end{aligned} \quad (6.5)$$

where

$$\overline{W}'_{kj}(\omega) = \text{Re}[\widehat{W}_{kj,kj}(\omega)] = \frac{|c|^2 t_c^{-1} (V_{kk} - V_{jj})^2}{(\omega - \omega_{kj})^2 + t_c^{-2}}, \quad (6.6a)$$

$$\overline{W}''_{kj}(\omega) = \text{Im}[\widehat{W}_{kj,kj}(\omega)] = \frac{|c|^2 (V_{kk} - V_{jj})^2 (\omega - \omega_{kj})}{(\omega - \omega_{kj})^2 + t_c^{-2}}. \quad (6.6b)$$

On the other hand, if the relaxation of  $S$  obeys the PTOC master equation, making use of Eq. (2.15) of paper I and (6.3), we have

$$\hat{R}_{ml,kj}(t) = |c|^2 t_c (V_{kk} - V_{jj})^2 (1 - e^{-t/t_c}) \delta_{mk} \delta_{lj} \quad (6.7)$$

and

$$\Omega_{kj}(t) = - |c|^2 t_c^2 (V_{kk} - V_{jj})^2 (1 - t/t_c - e^{-t/t_c}) \quad (6.8)$$

which, substituted into Eq. (5.2), gives us for the PTOC spectral profile

$$I^P(\omega) \propto \sum_{\substack{j,k \\ k>j}} \sigma_j^0 |\mu_{kj}(0)|^2 \text{Re} \left[ \int_0^\infty dt e^{i(\omega - \omega_{kj})t} \exp[|c|^2 t_c^2 (V_{kk} - V_{jj})^2 (1 - t/t_c - e^{-t/t_c})] \right]. \quad (6.9)$$

Thus, while the TTOC spectral line shape (6.5) consists of a sum of spectral lines similar to those obtained for a two-state jump model,<sup>7</sup> Eq. (6.9) gives the PTOC spectral line shape as a sum of spectral lines similar to those obtained for a system whose frequency carries out a stationary Gaussian process.<sup>7</sup> In the Markovian limit ( $t_c \rightarrow 0$ ,  $|c|^2 \rightarrow \infty$ ,  $t_c |c|^2 = \text{const}$ ) it is clear that Eqs. (6.5) and (6.9) lead to the Lorentzian profile (3.9) with

$$\Gamma_{kj} = |c|^2 t_c (V_{kk} - V_{jj})^2. \quad (6.10)$$

Equations (6.5) and (6.9) have been already obtained for a two-level system.<sup>8</sup> (In our case the  $j, k$  summation appears because we deal with a multilevel system with  $H'$  diagonal.) An interesting microscopic comparison of the two-level system equations can be seen in Ref. 9.

#### B. Interaction between consecutive levels

Let us suppose that the interaction Hamiltonian is such that

$$H'_{kj} = H'_{j+1,j} \delta_{k,j+1} + H'_{j-1,j} \delta_{k,j-1}, \quad (6.11)$$

i.e.,  $H'$  only couples consecutive levels. Let us also assume that the dipolar moment operator  $\mu(0)$  obeys the following selection rule:

$$\mu_{kj}(0) = \mu(f_j \delta_{k,j+1} + g_j \delta_{k,j-1}), \quad (6.12)$$

where  $f_j$  and  $g_j$  are coefficients that depend on  $j$ . The substitution of Eq. (6.12) into Eq. (4.2a) allows us to obtain for the TTOC absorption profile in the secular approximation

$$I_0^T(\omega) \propto -\mu^2 \sum_j f_j^2 \sigma_j^0 \text{Im}[\Lambda_{j+1,j}(\omega)], \quad (6.13a)$$

where, in agreement with Eqs. (4.2b)

$$\Lambda_{j+1,j}(\omega) = \frac{1}{(\omega - \omega_{j+1,j}) + \overline{\widehat{W}}_{j+1,j;j+1,j}(\omega)} \quad (6.13b)$$

and [see Eq. (4.2) of paper I]

$$\overline{\widehat{W}}_{j+1,j;j+1,j}(\omega) = J_{j+1,j+2;j+2,j+1}(\omega - \omega_{j+2,j}) + J_{j+1,j;j+1,j+1}(\omega) + J_{j,j+1;j+1,j}^*(-\omega) + J_{j,j-1;j-1,j}^*(\omega_{j+1,j-1} - \omega). \quad (6.13c)$$

On the other hand, substituting Eq. (6.12) into Eq. (4.9) and neglecting the indices ( $m, l$ ) that correspond to negative frequencies  $\omega_{ml}$  [we assume that the absorption spectrum ( $\omega$  positive) does not overlap with the emission spectrum ( $\omega$  negative)], the following TTOC interference profile is obtained:

$$I_1^T(\omega) \propto \mu^2 \sum_j f_j \sigma_j^0 \sum_{\substack{m \\ m \neq j+1}} g_m \text{Re}[\overline{\widehat{W}}_{m,m-1;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{m,m-1}(\omega)]. \quad (6.14)$$

For the interaction Hamiltonian (6.11), the only nonzero matrix elements  $\overline{\widehat{W}}_{ml,kj}(\omega)$  are those for which, once the indices ( $k, j$ ) have been fixed, the ( $m, l$ ) pair takes the values

$$(m, l) = (k, j), (k, j \pm 2), (k \pm 2, j), (k \pm 1, j \pm 1) \quad (6.15a)$$

and

$$(m, l) = (j, k) \Leftrightarrow k = j \pm 1. \quad (6.15b)$$

Then Eq. (6.14) takes the form

$$I_1^T(\omega) \propto \mu^2 \sum_j f_j \sigma_j^0 \{ g_j \text{Re}[\overline{\widehat{W}}_{j,j-1;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{j,j-1}(\omega)] + g_{j+2} \text{Re}[\overline{\widehat{W}}_{j+2,j+1;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{j+2,j+1}(\omega)] \}, \quad (6.16a)$$

where, making use of Eq. (4.4) of paper I,

$$\overline{\widehat{W}}_{j,j-1;j+1,j}(\omega) = -[J_{j,j-1;j+1,j}(\omega) + J_{j+1,j;j-1,j}^*(\omega_{j+1,j-1} - \omega)], \quad (6.16b)$$

$$\overline{\widehat{W}}_{j+2,j+1;j+1,j}(\omega) = -[J_{j,j+1;j+2,j+1}(\omega - \omega_{j+2,j}) + J_{j+1,j+2;j+1,j}^*(-\omega)]. \quad (6.16c)$$

Each of the terms appearing in Eq. (6.16a) gives the influence on the absorption line  $j \rightarrow j+1$  of its two adjacent absorption lines  $j-1 \rightarrow j$  and  $j+1 \rightarrow j+2$ , respectively.

For low-frequency spectra, it may happen that the positive coherences of  $\sigma(t)$  evolve mixed with the populations and with the negative coherences and, in general, the use of Eqs. (4.7) and (5.6) is no longer possible. Nevertheless, in this

particular example, the interaction Hamiltonian (6.11) does not couple the evolutions of the coherences with those of the populations and, therefore, Eqs. (4.7) and (5.6) are still applicable. In this case, in the interference profile (4.9) a new contribution will appear:

$$\begin{aligned} & \mu^2 \sum_j f_j \sigma_j^0 \{ f_{j+1} \text{Re}[\widehat{W}_{j+1,j+2;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{j+1,j+2}(\omega)] \\ & + f_j \text{Re}[\widehat{W}_{j,j+1;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{j,j+1}(\omega)] + f_{j-1} \text{Re}[\widehat{W}_{j-1;j+1,j}(\omega) \Lambda_{j+1,j}(\omega) \Lambda_{j-1,j}(\omega)] \} . \end{aligned} \quad (6.17)$$

For a given  $j$ , each term of this sum contains an antiresonant factor [due to the fact that the indices  $(m, l)$  in Eq. (4.9) can correspond to negative frequencies  $\omega_{ml}$ ] and gives, respectively, the contribution to the absorption line  $j \rightarrow j+1$  from the emission lines  $j+2 \rightarrow j+1$ ,  $j+1 \rightarrow j$ , and  $j \rightarrow j-1$ . In the case of the analysis of the PTOC interference profile, given by Eq. (5.8), the same procedure could be used.

## VII. SUMMARY

The relationship (2.11) between the functions  $\langle \mu_{jk}(t) \rangle$  with  $j \neq k$ , and the functions  $\sigma_m^{(jk)}(t)$  with  $l \neq m$ , reduces the calculation of the dipolar profile of  $S \oplus B$  to the study of the relaxation of  $S$  in  $B$ , when this relaxation is described in terms of the  $S$  reduced-density operator  $\sigma(t)$ . For simplicity we have supposed a nondegenerate and nonequidistant energy spectrum for  $S$ .

The sufficient conditions (3.7) of paper I for applying the secular approximation correspond, in the spectroscopic framework, to the isolation of the resonances (lines). In this case, if  $S$  evolves in the Markovian limit, the Lorentzian profile (3.2) is obtained. If, on the other hand,  $S$  evolves following the TTOC or PTOC schemes, the cor-

responding profiles are given by Eqs. (4.2) or (5.2), respectively.

The domain of application of the iterative methods developed in paper I for the study of the coherences when there exists a small mixing between their time evolution corresponds, in the spectroscopic framework, to the profile of a weak overlapping between resonances. In this case there is an interference line effect, which in the TTOC and PTOC schemes, gives rise to a correcting profile given by Eqs. (4.9) and (5.5), respectively. The overlapping between resonances is a sufficient, but not necessary, condition for the existence of interference effects. Thus, in the case of diagonal interaction (see Sec. VIA) the profile is always additive, independent of the vicinity between resonances.

## APPENDIX: CONNECTION BETWEEN THE MATRIX ELEMENTS OF THE ORDERED EXPONENTIALS

Let us consider the ordered exponential<sup>10</sup>

$$\begin{aligned} \widehat{A}(t) &= \exp_{-t} \left[ -i \int_0^t dt_1 \mathcal{L}'(t_1) \right] \\ &\equiv \widehat{\mathbb{1}} + (-i) \int_0^t dt_1 \mathcal{L}'(t_1) + (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{L}'(t_1) \mathcal{L}'(t_2) + \cdots \\ &\quad + (-i)^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \mathcal{L}'(t_1) \cdots \mathcal{L}'(t_n) + \cdots , \end{aligned} \quad (A1)$$

where

$$\mathcal{L}'(t) = e^{i\mathcal{L}_0 t} \mathcal{L}' e^{-i\mathcal{L}_0 t} \quad (A2)$$

and  $\widehat{\mathbb{1}}$  is the unity superoperator in the Liouville space of  $S \oplus B$ . In the ordered exponential  $\exp_{-t}$ , the superoperators  $\mathcal{L}'(t)$  are arranged in decreasing order of the values of the parameter  $t$ . Since  $\mathcal{L}_0$  and  $\mathcal{L}'$  are Hermitian superoperators, the Hermitian conjugate of the superoperator  $\widehat{A}(t)$  may be written as

$$\begin{aligned} \widehat{A}^\dagger(t) &= \widehat{\mathbb{1}} + i \int_0^t dt_1 \mathcal{L}'(t_1) + i^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{L}'(t_2) \mathcal{L}'(t_1) + \cdots + i^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \mathcal{L}'(t_n) \cdots \mathcal{L}'(t_1) + \cdots \\ &\equiv \exp_t \left[ i \int_0^t dt_1 \mathcal{L}'(t_1) \right] \end{aligned} \quad (A3)$$

which defines the ordered exponential

$$\exp_t \left[ i \int_0^t dt_1 \mathcal{L}'(t_1) \right]$$

in which, opposite to the development (A1), the  $\mathcal{L}'(t)$  superoperators are arranged in increasing order of the values of the parameter  $t$ .

Taking in Eq. (A3) the matrix elements in the representation of the eigenstates of  $H_0$  ( $H_0 = H_S + H_B$ ), we have

$$\begin{aligned} \hat{A}_{ab,cd}^\dagger(t) = & \delta_{ac}\delta_{bd} + i \int_0^t dt_1 \tilde{\mathcal{L}}'_{ab,cd}(t_1) + i^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \{ \tilde{\mathcal{L}}'(t_1) \tilde{\mathcal{L}}'(t_2) \}_{ab,cd} \\ & + \cdots + i^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \{ \tilde{\mathcal{L}}'(t_1) \cdots \tilde{\mathcal{L}}'(t_n) \}_{ab,cd} + \cdots, \end{aligned} \quad (\text{A4})$$

where we designate by  $a, b, c, d$  eigenstates of  $H_0$ . Furthermore, the diagonality of the superoperators  $\mathcal{L}_0$  yields

$$\begin{aligned} (ab | e^{i\mathcal{L}_0 t} | cd) & \equiv (e^{i\mathcal{L}_0 t})_{ab,cd} \\ & = (e^{i\mathcal{L}_0 t})_{ab,ab} \delta_{ac} \delta_{bd} \\ & = (e^{-i\mathcal{L}_0 t})_{ba,ba} \delta_{ac} \delta_{bd} \end{aligned} \quad (\text{A5})$$

while the matrix elements of  $\mathcal{L}'$  fulfill the relationship

$$\mathcal{L}'_{ab,cd} = \hbar^{-1} (H'_{ac} \delta_{bd} - H'_{ab} \delta_{ac}) = -\mathcal{L}'_{dc,ba}. \quad (\text{A6})$$

Making use of Eqs. (A5) and (A6), the different matrix elements which appear in the development (A4) may be written as

$$\tilde{\mathcal{L}}'_{ab,cd}(t_1) = -\tilde{\mathcal{L}}'_{dc,ba}(t_1), \quad (\text{A7a})$$

$$\{ \tilde{\mathcal{L}}'(t_2) \tilde{\mathcal{L}}'(t_1) \}_{ab,cd} = \{ \tilde{\mathcal{L}}'(t_1) \tilde{\mathcal{L}}'(t_2) \}_{dc,ba}, \quad (\text{A7b})$$

$$\vdots$$

$$\{ \tilde{\mathcal{L}}'(t_n) \cdots \tilde{\mathcal{L}}'(t_1) \}_{ab,cd} = (-1)^n \{ \tilde{\mathcal{L}}'(t_1) \cdots \tilde{\mathcal{L}}'(t_n) \}_{dc,ba}. \quad (\text{A7c})$$

Substituting expression (A7) into the development (A4) and comparing the result obtained with the matrix elements of (A1), we have the relationship

$$\hat{A}_{ab,cd}^\dagger(t) = \hat{A}_{dc,ba}(t) \quad (\text{A8})$$

used in Sec. II.

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