Dynamics of stochastic systems in nonlinear optics. II. The case of a stochastic configuration interaction

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In the preceding paper we have developed a formal theoretical approach to describe the dynamics of stochastic systems in nonlinear optics. The main emphasis has been on the description of the equation of motion of the free system, since the optical fields are usually treated by perturbation expansion. Here we explicitly develop the dynamics of complex models, which should be helpful in realistic situations. Two different models are considered. The dynamics of a stochastic three-level system is introduced first. Then the case of two configurations stochastically coupled is explicitly treated. This last model is of interest in order to understand the effects of nonradiative transitions on the nonlinear-optical properties of stochastic systems.
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I. INTRODUCTION

The study of nonlinear-optical processes like two-photon absorption [1], the dynamical Stark effect [2,3], or the different types of wave mixing [4] has gained considerable interest in recent decades. One important motivation for these developments comes from the fact that they provide information about the ability of materials to offer better or new possibilities in optoelectronics. Alongside the developments that have taken place in the field of inorganic semiconductor materials [5], today, organic compounds offer an interesting alternative for future applications [6,7]. Because of the large variety of organic materials, as well as the development of newly synthesized compounds, it becomes very important to define criteria to select, in some way, the system which fits best the applications of interest.

For many years, spectroscopic methods have been used to study the internal dynamics of material systems and information that has been obtained from the analysis of the absorbed or emitted light. At that time, most of the descriptions and experiments were concerned with optical methods in the linear regime. They have been very helpful in showing that nonradiative transitions deeply affect the dynamics induced by an external optical field in a molecular compound [8–10]. In fact, a tremendous number of works have been devoted to the evaluation of nonradiative decay rates associated with electronic or vibrational relaxation processes. They were as different as the energy dependence of electronic relaxation processes [11,12], the search for criteria for irreversible electronic transitions [13,14], the dependence of these criteria on the nature of the nonradiative processes under consideration, or even the real nature of the true molecular eigenstate [15]. When these studies were developed, little attention had been paid to the dephasing processes which can take place during the course of nonradiative transitions [16]. For this reason, all the studies were done in Hilbert space and are inadequate for more general descriptions involving dephasing. Therefore, the problem of how a dephasing process affects a nonradiative transition is still an open question. In addition, concerning these previous descriptions, the interaction responsible for the nonradiative transitions has always been considered as a purely quantum interaction which depends on the particular process of interest, such as internal conversion, intersystem crossing, etc. It results from these observations that a realistic description of these processes is a big challenge, in part because the required Liouvillian formalism implies a Liouville representation whose dimension corresponds to the square of the one needed in Hilbert space, but also because in this representation the structure of the coupling is much more intricate. This makes the matrix inversion, always a necessary step in the resolvent technique [17], very difficult.

More recently, there has been a burst of developments in the field of dynamics of stochastic systems [18]. Stochasticity has been a very helpful concept in tackling problems as varied as the energy transfer in molecular crystals [19,20] and the occurrence of interactions in the intermediate states during the course of resonant second-order optical processes [21,22]. It has to be noted that an interesting consequence of the statistical distribution of the stochastic interactions is a decoupling of the dynamical equations of the averaged density-matrix elements as opposed to the microscopic quantum case. Therefore, a study of the internal dynamics of a system induced by stochastic couplings and undergoing dephasing processes can be carried out [17]. The study of localization and dephasing effects in a time-dependent Anderson Hamiltonian done by Wolynes and co-workers [23] is a striking example of the interplay of these two processes. However, in this work, the enhancement of transport by dephasing for states which are localized in the absence of dephasing and the inhibition of transport for delocalized states has only been established numerically. The search for an analytical solution is, of course, desirable.

It is the goal of this work to present an analytical description of two applications which are relevant to a stochastic approach to nonradiative transitions. By taking advantage of the formalism presented in the preceding paper [17], hereafter referred to as I, we present in Sec. II the study of the dynamics induced by stochastic perturbations in a three-level system undergoing relaxation and dephasing processes. This description is valid in the Markovian or the weakly colored noise cases. For the sake of simplicity, in the latter case, the various constants have not been expressed in terms of the various correlation time ϵ_i^{-1} of the stochastic parameters. However their introduction can be carried out straightforwardly if necessary. The free evolution needed in nonlinear optics for any type of study based on perturbation expansions has been explicitly developed. Section III is devoted to a particular model frequently encountered in the study of nonradiative transitions in molecular systems. The peculiarity of our model consists in using a stochastic interaction to couple the radiant state to the isoenergetic nonradiant configuration. Then, relaxation and absorption spectra are evaluated and discussed in the last section.

II. DYNAMICS INDUCED BY STOCHASTIC PERTURBATIONS IN A THREE-LEVEL SYSTEM

Recently, we have developed the dynamics of a three-level system in order to analyze how a third nonradiant state can affect the nonlinear-optical properties of an optical transition [24]. From this model, it was established that the quantum interaction enhances the optical nonlinearities. A stochastic counterpart of this model is developed here. It will be very suitable to describe, for example, the occurrence of fluctuations in the intermediate states during the course of a resonant second-order optical process, as observed in β carotene [21,22]. However, only the Markovian and the weakly colored noise cases will be considered here.

The starting point of any dynamical study of a system undergoing stochastic quantum perturbations is the equation of motion of the average density matrix [25–27]. It takes the form

$$\frac{d\langle\rho^s(t)\rangle}{dt}=-\frac{i}{\hbar}[L_s+R(t)]\langle\rho^s(t)\rangle , \quad (2.1)$$

where $L_s=[H_s,\ ]$ is the Liouvillian of the system with a zeroth-order Hamiltonian

$$H_s=\alpha J_3+\beta J_8 \quad (2.2)$$

and an interaction Hamiltonian

$$\tilde{H}(t)=\sum_{i=1}^{8}\hbar\tilde{\Phi}_i(t)J_i \quad (2.3)$$

described in terms of the SU(3) generators J_i ($i=1,8$) given in Appendix A. Moreover, the stochastic variables $\tilde{\Phi}_i(t)$ satisfy the statistical properties defined by the relations [28]

$$\langle\tilde{\Phi}_i(t)\rangle=0 ,$$
$$\langle\tilde{\Phi}_i(t)\tilde{\phi}_j(\tau)\rangle=\lambda_i\frac{\epsilon_i}{2}e^{-\epsilon_i|t-\tau|}\delta_{ij} \quad (2.4)$$

which correspond to Gaussian, non-δ-correlated energy interactions. For the sake of convenience, we have introduced the operator

$$R(t)=-i\hbar[\Gamma_s(t)+\Gamma(t)] . \quad (2.5)$$

The Liouville operator $\Gamma_s(t)$ accounts for the stochastic properties of the system and its properties have been discussed extensively in previous papers [17,25,26]. Similarly, the damping operator $\Gamma(t)$ describes spontaneous emission like any other purely dissipative effect of the baths coupled to the system. While $\Gamma(t)$ will always be assumed to be purely Markovian the stochastic operator $\Gamma_s(t)$ will be described either in the Markovian or in the weakly colored noise limits [17]. Both cases can be handled easily because the time dependence of $\Gamma_s(t)$ can then be neglected.

From the formal development

$$\langle\rho^s(t)\rangle=\sum_{i=0}^{N^2-1}M_i(t)J_i \quad (2.6)$$

and the commutation properties of the generators J_i, the general equations of motion take the form

$$\frac{dM_j(t)}{dt}=-\sum_{i=1}^{8}K_{ji}(t)M_i(t)-K_{j0} , \quad (2.7)$$

where the nonzero K_{ij} coefficients are given in the Appendix B. We still have to relate the parameters α and β of relation (2.2) to the transition frequencies

$$\begin{aligned}\hbar\omega_{21}&=-2\alpha ,\\ \hbar\omega_{31}&=-\alpha-\beta\sqrt{3} ,\\ \hbar\omega_{32}&=\alpha-\beta\sqrt{3} ,\end{aligned} \quad (2.8)$$

where the notation $\omega_{ij}=(E_i-E_j)/\hbar$ has been used. We can check on this simple model that the structure of the set of differential equations (2.7) satisfies the general properties previously established [17]. Moreover, a great simplification resulting from the Markovian limit or from the weakly colored noise limit is obvious here. With these assumptions, formal solutions to the equation set (2.7) are obtained by the Laplace transform. For the three-level system, the differential equations are coupled pairwise. Any given set of equations can be written:

$$\begin{aligned}(p+K_{ii})\hat{M}_i(p)+K_{ij}\hat{M}_j(p)&=M_i(0)-K_{i0}\frac{1}{p} ,\\ K_{ji}\hat{M}_i(p)+(p+K_{jj})\hat{M}_j(p)&=M_j(0)-K_{j0}\frac{1}{p} ,\end{aligned} \quad (2.9)$$

where $\hat{M}_i(p)$ represents the Laplace transform of $M_i(t)$. The solutions are given by

$$\hat{M}_i(p)=\frac{[pM_i(0)-K_{i0}](p+K_{jj})-K_{ij}[pM_j(0)-K_{j0}]}{p(p-\lambda_{ij}^+)(p-\lambda_{ij}^-)} , \quad (2.10)$$

$$\hat{M}_j(p)=\frac{[pM_j(0)-K_{j0}](p+K_{ii})-K_{ji}[pM_i(0)-K_{i0}]}{p(p-\lambda_{ij}^+)(p-\lambda_{ij}^-)}$$

with

$$\lambda_{ij}^{+}=-\tfrac{1}{2}\{(K_{ii}+K_{jj})-[(K_{ii}-K_{jj})^2+4K_{ji}K_{ij}]^{1/2}\} ,$$

$$\lambda_{ij}^{-}=-\tfrac{1}{2}\{(K_{ii}+K_{jj})+[(K_{ii}-K_{jj})^2+4K_{ji}K_{ij}]^{1/2}\} . \tag{2.11}$$

From the inverse Laplace transform the final expressions for the coefficients $M_i(t)$ and $M_j(t)$ are deduced:

$$M_i(t)=M_{i0}+M_{i+}e^{\lambda_{ij}^{+}t}+M_{i-}e^{\lambda_{ij}^{-}t} ,$$

$$M_j(t)=M_{j0}+M_{j+}e^{\lambda_{ij}^{+}t}+M_{j-}e^{\lambda_{ij}^{-}t} , \tag{2.12}$$

where the indices i and j are pairwise coupled in the following way: $(i,j)=\{(1,2),(3,8),(4,5),(6,7)\}$. For any couple of indices (p,q) the M constants are given by

$$M_{p0}=\frac{-K_{p0}K_{qq}+K_{q0}K_{pq}}{\lambda_{pq}^{+}\lambda_{pq}^{-}} ,$$

$$M_{p+}=\frac{[\lambda_{pq}^{+}M_p(0)-K_{p0}](\lambda_{pq}^{+}+K_{qq})-K_{pq}[\lambda_{pq}^{+}M_q(0)-K_{q0}]}{\lambda_{pq}^{+}(\lambda_{pq}^{+}-\lambda_{pq}^{-})} , \tag{2.13}$$

$$M_{p-}=\frac{[\lambda_{pq}^{-}M_p(0)-K_{p0}](\lambda_{pq}^{-}+K_{qq})-K_{pq}[\lambda_{pq}^{-}M_q(0)-K_{q0}]}{\lambda_{pq}^{-}(\lambda_{pq}^{-}-\lambda_{pq}^{+})} .$$

In addition, when the pair of constants K_{p0} and K_{q0} are zero, we have no pole for $p=0$. Following the methodology developed in I, we still have to calculate the V matrix. It is defined by the relations

$$\langle\rho_{11}^{s}(0)\rangle=\tfrac{1}{3}+M_3(0)+\frac{1}{\sqrt{3}}M_8(0) ,$$

$$\langle\rho_{22}^{s}(0)\rangle=\tfrac{1}{3}-M_3(0)+\frac{1}{\sqrt{3}}M_8(0) ,$$

$$\langle\rho_{33}^{s}(0)\rangle=\tfrac{1}{3}-\frac{2}{\sqrt{3}}M_8(0) ,$$

$$\langle\rho_{12}^{s}(0)\rangle=M_1(0)-iM_2(0) , \tag{2.14}$$

$$\langle\rho_{13}^{s}(0)\rangle=M_4(0)-iM_5(0) ,$$

$$\langle\rho_{23}^{s}(0)\rangle=M_6(0)-iM_7(0) .$$

It must be noted that the three other matrix elements are deduced by complex conjugation, taking into account the real nature of the $M_i(t)$ coefficients. From these previous considerations, it appears that we have all the required information to calculate the free evolution of a stochastic three-level system. It is contained in the $G_{ijkl}(t,0)$ matrix elements which are necessary for any perturbation expansion, like those used in nonlinear optics. Their expressions are tedious. They are obtained from the identification of the $\langle\rho_{ij}^{s}(t)\rangle$ expressions with the formal development

$$\langle\rho_{ij}^{s}(t)\rangle=\sum_{p,q}G_{ijpq}(t,0)\langle\rho_{ij}^{s}(0)\rangle . \tag{2.15}$$

To this end, from relations (2.14), we extract the expressions of $M_j(0)$ for $j=1,8$. From the density-matrix elements associated with the populations

$$\begin{aligned}\langle\rho_{ii}^{s}(t)\rangle=&\Bigg[\tfrac{1}{3}+M_{30}+\frac{1}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{30}(\lambda_{38}^{+}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]\\&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{30}(\lambda_{38}^{-}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]\Bigg]\\&\times[\langle\rho_{11}^{s}(0)\rangle+\langle\rho_{22}^{s}(0)\rangle+\langle\rho_{33}^{s}(0)\rangle]\\&+\Bigg[\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[\lambda_{38}^{+}(\lambda_{38}^{+}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{+}\right]\\&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[\lambda_{38}^{-}(\lambda_{38}^{-}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{-}\right]\Bigg]\{\tfrac{1}{2}[\langle\rho_{11}^{s}(0)\rangle-\langle\rho_{22}^{s}(0)\rangle]\}\\&+\Bigg[\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]\\&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right]\Bigg]\left[\frac{\sqrt{3}}{6}[\langle\rho_{11}^{s}(0)\rangle+\langle\rho_{22}^{s}(0)\rangle-2\langle\rho_{33}^{s}(0)\rangle]\right]\end{aligned} \tag{2.16}$$

we get the elements $G_{1111}(t,0)$, $G_{1122}(t,0)$, and $G_{1133}(t,0)$. Their expressions are given in Appendix C. Similarly, the expression of the population $\langle \rho_{22}^{s}(t) \rangle$ is deduced from the one of $\langle \rho_{11}^{s}(t) \rangle$ by the simple change $M_{30} \rightarrow -M_{30}$ and $M_{3\mp} \rightarrow -M_{3\mp}$, and finally $\langle \rho_{33}^{s}(t) \rangle$ is obtained using the probability conservation

$$\sum_{i} \langle \rho_{ii}^{s}(t) \rangle = 1 \ . \tag{2.17}$$

They give the elements $G_{2211}(t,0)$, $G_{2222}(t,0)$, $G_{2233}(t,0)$ and $G_{3311}(t,0)$, $G_{3322}(t,0)$, $G_{3333}(t,0)$, respectively. Again, their expressions are developed in Appendix C. We still have to consider the expressions for the coherences. Using the explicit expressions of the coefficients $M_{i\pm}$ and taking into account that for homogeneous differential equations the coefficients K_{p0} and K_{q0} are zero in relation (2.13), we have no pole for $p=0$. Consequently, the coherences take the form

$$\begin{aligned} \langle \rho_{ij}^{s}(t) \rangle = {} & \frac{e^{\lambda_{ij}^{+} t}}{\lambda_{ij}^{+}(\lambda_{ij}^{+}-\lambda_{ij}^{-})} \{ [\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{jj}) + iK_{ji}\lambda_{ij}^{+}] M_i(0) + [-K_{ij}\lambda_{ij}^{+} - i\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{ii})] M_j(0) \} \\ & + \frac{e^{\lambda_{ij}^{-} t}}{\lambda_{ij}^{-}(\lambda_{ij}^{-}-\lambda_{ij}^{+})} \{ [\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{jj}) + iK_{ji}\lambda_{ij}^{+}] M_i(0) + [-K_{ij}\lambda_{ij}^{-} - i\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{ii})] M_j(0) \} \ . \end{aligned} \tag{2.18}$$

If we introduce the expressions

$$\begin{aligned} & M_i(0) = \tfrac{1}{2}[\langle \rho_{ij}^{s}(0) \rangle + \langle \rho_{ji}^{s}(0) \rangle] \ , \\ & M_j(0) = \frac{1}{2i}[\langle \rho_{ji}^{s}(0) \rangle - \langle \rho_{ij}^{s}(0)] \end{aligned} \tag{2.19}$$

the matrix elements are easily deduced:

$$\begin{aligned} G_{ijij}(t,0) = {} & \frac{e^{\lambda_{ij}^{+} t}}{\lambda_{ij}^{+}(\lambda_{ij}^{+}-\lambda_{ij}^{-})} \left[\tfrac{1}{2}[\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{jj}) + iK_{ji}\lambda_{ij}^{+}] + \frac{1}{2i}[K_{ij}\lambda_{ij}^{+} + i\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{ii})] \right] \\ & + \frac{e^{\lambda_{ij}^{-} t}}{\lambda_{ij}^{-}(\lambda_{ij}^{-}-\lambda_{ij}^{+})} \left[\tfrac{1}{2}[\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{jj}) + iK_{ji}\lambda_{ij}^{-}] + \frac{1}{2i}[K_{ij}\lambda_{ij}^{-} + i\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{ii})] \right] \end{aligned} \tag{2.20}$$

and we have the additional relation

$$G_{ijij}(t,0) = G_{jiji}^{*}(t,0) \ . \tag{2.21}$$

Following the same procedure, we also get

$$\begin{aligned} G_{ijji}(t,0) = {} & \frac{e^{\lambda_{ij}^{+} t}}{\lambda_{ij}^{+}(\lambda_{ij}^{+}-\lambda_{ij}^{-})} \left[\tfrac{1}{2}[\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{jj}) + iK_{ji}\lambda_{ij}^{+}] - \frac{1}{2i}[K_{ij}\lambda_{ij}^{+} + i\lambda_{ij}^{+}(\lambda_{ij}^{+}+K_{ii})] \right] \\ & + \frac{e^{\lambda_{ij}^{-} t}}{\lambda_{ij}^{-}(\lambda_{ij}^{-}-\lambda_{ij}^{+})} \left[\tfrac{1}{2}[\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{jj}) + iK_{ji}\lambda_{ij}^{-}] - \frac{1}{2i}[K_{ij}\lambda_{ij}^{-} + i\lambda_{ij}^{-}(\lambda_{ij}^{-}+K_{ii})] \right] \end{aligned} \tag{2.22}$$

again, with the following symmetry relation

$$G_{jiij}(t,0) = G_{ijji}^{*}(t,0) \ . \tag{2.23}$$

It is not our aim here to enter into a more detailed study of such systems. However, it is quite obvious that any field, like those used in nonlinear optics for instance, treated by a perturbation expansion requires the knowledge of the free evolution of the system alone. Then, all the problems of this type can be handled straightforwardly on a stochastic three-level system in the Markovian or the weakly colored noise case. In Sec. II we will emphasize more on the internal dynamics of the material system.

III. STOCHASTIC CONFIGURATION INTERACTION

For many years, the Freed-Jortner model [29] has played a central role as a prototype in the study of nonradiative decay in organic compounds. This model is based on a quantum interaction which depends on the nature of the nonradiative transitions. Stochastic approaches offer an interesting alternative to the description of these processes. In addition, the simplification resulting from the statistical distribution enables the introduction of the dephasing processes. As previously mentioned, we will be concerned by the Markovian or the weakly colored noise cases. Also, for the sake of convenience, we introduce the stochasticity in terms of the correlation function of the interaction

$$\langle \tilde{H}_{ij}(t)\tilde{H}_{kl}(s)\rangle = \hbar^2\lambda_{ijkl}\frac{\epsilon_{ijkl}}{2}e^{-\epsilon_{ijkl}|t-s|} , \quad (3.1)$$

where the constant is defined by

$$\lambda_{ijkl}=\lambda_{ijji}\delta_{il}\delta_{jk} . \quad (3.2)$$

This characterization has the advantage over the previous definitions of keeping the various stochastic variables completely independent so that diagonal as well as nondiagonal stochastic coupling can be treated simultaneously on the same footing. Also, we observe the same decoupling in the equation of motion of the populations and coherences. We still need the explicit expressions of the stochastic operator $R_s(t)$ which drives the evolution of the average density matrix of the system alone. It takes the form

$$\begin{aligned}[R_s(t)\langle\rho(t)\rangle]_{ij} = -\frac{i\hbar}{2}\sum_p \Bigg\{ &\lambda_{ippi}\epsilon_{ippi}\frac{1-e^{-(\epsilon_{ippi}+i\omega_{pi})t}}{\epsilon_{ippi}+i\omega_{pi}}\langle\rho(t)\rangle_{ij} - \lambda_{piip}\delta_{ij}\epsilon_{piip}\frac{1-e^{-(\epsilon_{piip}+i\omega_{ip})t}}{\epsilon_{piip}+i\omega_{ip}}\langle\rho(t)\rangle_{pp} \\ &-\lambda_{ippi}\delta_{ij}\epsilon_{ippi}\frac{1-e^{-(\epsilon_{ippi}+i\omega_{pi})t}}{\epsilon_{ippi}+i\omega_{pi}}\langle\rho(t)\rangle_{pp} + \lambda_{pjjp}\epsilon_{pjjp}\frac{1-e^{-(\epsilon_{pjjp}+i\omega_{jp})t}}{\epsilon_{pjjp}+i\omega_{jp}}\langle\rho(t)\rangle_{ij}\Bigg\} . \end{aligned} \quad (3.3)$$

After some simplifications, its matrix elements can be expressed as

$$\Gamma_{s\,ij\,pq}(t)=\Gamma^{(1)}_{s\,ij\,pq}(t)+\Gamma^{(2)}_{s\,ij\,pq}(t) , \quad (3.4)$$

where

$$\begin{aligned}\Gamma^{(1)}_{s\,ij\,pq}(t) &= \frac{1}{2}\sum_l \left[\lambda_{illi}\epsilon_{illi}\frac{1-e^{-(\epsilon_{illi}+i\omega_{li})t}}{\epsilon_{illi}+i\omega_{li}} + \lambda_{ljjl}\epsilon_{ljjl}\frac{1-e^{-(\epsilon_{ljjl}+i\omega_{jl})t}}{\epsilon_{ljjl}+i\omega_{jl}}\right]\delta_{ip}\delta_{jq} , \\ \Gamma^{(2)}_{s\,ij\,pq}(t) &= -\frac{1}{2}\left[\lambda_{piip}\epsilon_{piip}\frac{1-e^{-(\epsilon_{piip}+i\omega_{ip})t}}{\epsilon_{piip}+i\omega_{ip}} + \lambda_{ippi}\epsilon_{ippi}\frac{1-e^{-(\epsilon_{ippi}+i\omega_{pi})t}}{\epsilon_{ippi}+i\omega_{pi}}\right]\delta_{ij}\delta_{pq} . \end{aligned} \quad (3.5)$$

In the following, we will apply this approach to a material system where the essential part of the internal dynamics can be described by a radiant excited state coupled via a stochastic perturbation to a manifold of states of a lower electronic configuration shown in Fig. 1. Again, we will consider the evolution of the average density matrix by neglecting the time dependence of the $R_s(t)$ operator. The starting point of our description is, as usual, the Liouville equation:

$$\frac{\partial\langle\rho(t)\rangle}{\partial t} = -\frac{i}{\hbar}[L_s+R_s(t)]\langle\rho(t)\rangle - \Gamma\langle\rho(t)\rangle , \quad (3.6)$$

where the relaxation and the dephasing processes have been accounted for. With our previous assumption, the Laplace transform of relation (3.6) is written as

$$p\langle\tilde{\rho}\rangle - \langle\rho(0)\rangle = -\frac{i}{\hbar}L_s\langle\tilde{\rho}\rangle - \Gamma_s\langle\tilde{\rho}\rangle - \Gamma\langle\tilde{\rho}\rangle , \quad (3.7)$$

where $\langle\tilde{\rho}\rangle$ stands for the Laplace transform

$$\langle\tilde{\rho}\rangle = \int_0^\infty dt\, e^{-pt}\langle\rho(t)\rangle . \quad (3.8)$$

If we introduce, in the Liouville space, the projection operators $\mathcal{P}$ and $\mathcal{Q}$, this equation becomes

$$\begin{aligned} p\mathcal{P}\langle\tilde{\rho}\rangle - \mathcal{P}\langle\rho(0)\rangle &= -\frac{i}{\hbar}\mathcal{P}(L_s+R_s-i\hbar\Gamma)\mathcal{P}\mathcal{P}\langle\tilde{\rho}\rangle \\ &\quad -\frac{i}{\hbar}\mathcal{P}(L_s+R_s-i\hbar\Gamma)\mathcal{Q}\mathcal{Q}\langle\tilde{\rho}\rangle , \\ p\mathcal{Q}\langle\tilde{\rho}\rangle - \mathcal{Q}\langle\rho(0)\rangle &= -\frac{i}{\hbar}\mathcal{P}(L_s+R_s-i\hbar\Gamma)\mathcal{Q}\mathcal{Q}\langle\tilde{\rho}\rangle \\ &\quad -\frac{i}{\hbar}\mathcal{Q}(L_s+R_s-i\hbar\Gamma)\mathcal{P}\mathcal{P}\langle\tilde{\rho}\rangle \end{aligned} \quad (3.9)$$

with

$$\mathcal{P}L_s\mathcal{Q}=\mathcal{Q}L_s\mathcal{P}=0 .$$

By solving the equation set (3.9), we obtain the formal solution

$$Q\langle\tilde{\rho}\rangle=\frac{1}{p+\frac{i}{\hbar}Q[L_s+R_s-i\hbar\Gamma]Q}\left[Q\langle\rho(0)\rangle-\frac{i}{\hbar}Q(R_s-i\hbar\Gamma)\mathcal{P}\mathcal{P}\langle\tilde{\rho}\rangle\right] \tag{3.10}$$

and

$$\mathcal{P}\langle\tilde{\rho}\rangle=\left[p+\frac{i}{\hbar}\mathcal{P}(L_s+R_s-i\hbar\Gamma)\mathcal{P}-\frac{i}{\hbar}\mathcal{P}(R_s-i\hbar\Gamma)Q\frac{1}{p+\frac{i}{\hbar}Q(L_s+R_s-i\hbar\Gamma)Q}\frac{i}{\hbar}Q(R_s-i\hbar\Gamma)\mathcal{P}\right]^{-1}$$
$$\times\left[\mathcal{P}\langle\rho(0)\rangle-\frac{i}{\hbar}\mathcal{P}(R_s-i\hbar\Gamma)Q\frac{1}{p+\frac{i}{\hbar}Q(L_s+R_s-i\hbar\Gamma)Q}Q\langle\rho(0)\rangle\right], \tag{3.11}$$

which constitutes the restriction of the density matrix with respect to $\mathcal{P}$ and Q. In the space spanned by Q, the matrix elements can be developed into the form

$$\langle\langle\alpha\beta|p+\frac{i}{\hbar}QL_sQ+Q\Gamma_sQ+Q\Gamma Q|\lambda\mu\rangle\rangle=(p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\,\alpha\beta}+\Gamma_{\alpha\beta\,\alpha\beta})\delta_{\alpha\lambda}\delta_{\beta\mu}\,, \tag{3.12}$$

where the notation $R_s(t)=-i\hbar\Gamma_s(t)$ has been introduced. Therefore, the corresponding matrix representation is diagonal. Consequently, the factor included in the brackets of relation (3.11) is given by

$$\langle\langle mn|p+\frac{i}{\hbar}\mathcal{P}(L_s+R_s-i\hbar\Gamma)\mathcal{P}-\sum_{\alpha,\beta}\left[\frac{i}{\hbar}\mathcal{P}R_s|\alpha\beta\rangle\rangle+\mathcal{P}\Gamma|\alpha\beta\rangle\rangle\right]$$
$$\times\frac{1}{p+i\omega_{\alpha\beta}+\frac{i}{\hbar}R_{s\,\alpha\beta\,\alpha\beta}+\Gamma_{\alpha\beta\,\alpha\beta}}\left[\frac{i}{\hbar}\langle\langle\alpha\beta|R_s\mathcal{P}+\langle\langle\alpha\beta|\Gamma\mathcal{P}\right]|uv\rangle\rangle\,. \tag{3.13}$$

To simplify the notation, we introduce Latin letters for the kets $|ij\rangle\rangle$ of the $\mathcal{P}$ space and Greek letters for those of the Q space. In order to calculate the inverse of the matrix given by relation (3.13), we write it as

$$A=\begin{bmatrix}a_{1111} & 0 & 0 & \Gamma_{11\,22}\\ 0 & a_{1212} & 0 & 0\\ 0 & 0 & a_{2121} & 0\\ \Gamma_{22\,11} & 0 & 0 & a_{2222}\end{bmatrix}, \tag{3.14}$$

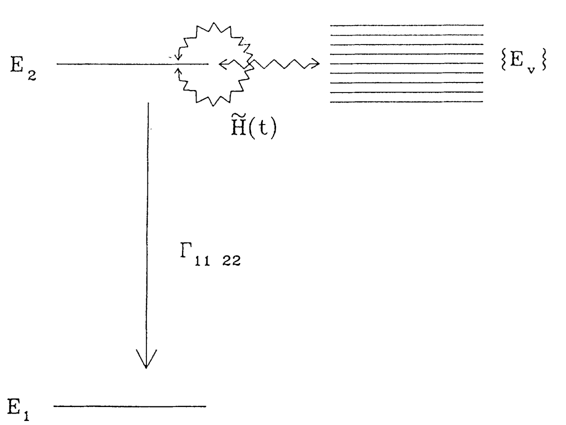

FIG. 1. Energy-level scheme of the material system: the diagonal perturbation generates frequency modulation while nondiagonal perturbations between states $|2\rangle$ and $\{|v\rangle\}$ induce equipartition of the populations.

where

$$a_{1111}=p+\Gamma_{s\,11\,11}+\Gamma_{11\,11}\,,$$
$$a_{1212}=p+i\omega_{12}+\Gamma_{s\,12\,12}+\Gamma_{12\,12}\,,$$
$$a_{2121}=p+i\omega_{21}+\Gamma_{s\,21\,21}+\Gamma_{21\,21}\,,$$
$$a_{2222}=p+\Gamma_{s\,22\,22}+\Gamma_{22\,22}-\sum_v\frac{\Gamma_{s\,22\,vv}\Gamma_{s\,vv\,22}}{p+\Gamma_{s\,vv\,vv}}\,.$$

The energy-level scheme has been given in Fig. 1. Also, we have introduced the simplifying assumptions

$$\Gamma_{11\,11}\simeq\Gamma_{22\,11}\simeq\Gamma_{11\,vv}\simeq\Gamma_{22\,vv}\simeq\Gamma_{vv\,v'v'}\simeq 0$$

because we just want to retain in the internal dynamics the influence of the manifold of states on the radiant state $|2\rangle$. Then, the determinant takes the simple form

$$\det A=p(p+i\omega_{12}+\Gamma_{12\,12})(p+i\omega_{21}+\Gamma_{21\,21}$$
$$\times\left[p+\Gamma_{22\,22}+\Gamma_{s\,22\,22}-\sum_v\frac{\Gamma_{s\,22\,vv}\Gamma_{s\,vv\,22}}{p+\Gamma_{s\,vv\,vv}}\right]. \tag{3.15}$$

The time evolution of $\mathcal{P}\langle\rho(t)\rangle$ will require the inverse Laplace transform of $\mathcal{P}\langle\tilde{\rho}\rangle$. As is well known, its integral relation will have three roots:

$$p_1=0\,,$$
$$p_2=-i\omega_{12}-\Gamma_{12\,12}-\Gamma_{s\,12\,12}\,, \tag{3.16}$$
$$p_3=-i\omega_{21}-\Gamma_{21\,21}-\Gamma_{s\,21\,21}$$

plus the additional roots provided by the solutions of

$$p+\Gamma_{22\,22}+\Gamma_{s\,22\,22}-\sum_{v}\frac{\Gamma_{s\,22\,vv}\Gamma_{s\,vv\,22}}{p+\Gamma_{s\,vv\,vv}}=0 \; . \tag{3.17}$$

The distribution of these roots will depend on the energetic structure of the levels $|v\rangle$. Taking into account the symmetry rules of the Γ_s operator [16], we have

$$\Gamma_{s\,22\,22}=-\sum_{v}\Gamma_{s\,22\,vv} \; .$$

In the same way, since $\Gamma_{s\,vv\,22}=\Gamma_{s\,22\,vv}$, we get

$$\Gamma_{s\,vv\,vv}=-\sum_{m\,(\neq v)}\Gamma_{s\,vv\,mm}=-\Gamma_{s\,vv\,22} \; .$$

If all the $\Gamma_{s\,vv\,vv}$ are identical to each other and if this is still true for the $\Gamma_{s\,vv\,22}$, then relation (3.17) gives two additional roots:

$$p_{4,5}=-\tfrac{1}{2}(\Gamma_{22\,22}+\Gamma_{s\,22\,22}+\Gamma_{s\,vv\,vv})\pm\tfrac{1}{2}\{(\Gamma_{2222}+\Gamma_{s\,2222}+\Gamma_{s\,vvvv})^2-4[(\Gamma_{2222}+\Gamma_{s\,2222})\Gamma_{s\,vvvv}-N\Gamma_{s\,22vv}\Gamma_{s\,vv22}]\}^{1/2} \; .$$

We are now ready to calculate the various matrix elements of the Liouville operator $G(t,0)$ defined by

$$\rho_{ij}(t)=\sum_{p,q}G_{ijpq}(t,0)\rho_{pq}(0) \; . \tag{3.18}$$

It gives the evolution of the free system, which is required in most of the calculations in nonlinear optics. To this end, we begin by calculating the matrix elements of $\langle\tilde{\rho}\rangle$. If the couple (i,j) of indices pertains to $\mathcal{P}$, from Eq. (3.11) we have

$$\langle\tilde{\rho}\rangle_{ij}=[\mathcal{P}\langle\tilde{\rho}\rangle]_{ij}=\sum_{k,l}\frac{p+\Gamma_{s\,vvvv}}{\prod_{i=1}^{5}(p-p_i)}[{}^t(\text{cofact})]_{ijkl} \times\left[[\mathcal{P}\langle\rho(0)\rangle]_{kl}-\sum_{\alpha,\beta}\left[\frac{i}{\hbar}\mathcal{P}(R_s-i\hbar\Gamma)Q\right]_{kl\alpha\beta}\frac{1}{p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}[Q\langle\rho(0)\rangle]_{\alpha\beta}\right] , \tag{3.19}$$

while if the couple (α,β) belongs to Q, we get

$$\langle\tilde{\rho}\rangle_{\alpha\beta}=(Q\langle\tilde{\rho}\rangle)_{\alpha\beta}=\frac{1}{p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}\left[[Q\langle\rho(0)\rangle]_{\alpha\beta}-\sum_{i,j}\left[\frac{i}{\hbar}Q(R_s-i\hbar\Gamma)\mathcal{P}\right]_{\alpha\beta ij}(\mathcal{P}\langle\tilde{\rho}\rangle)_{ij}\right] . \tag{3.20}$$

We still have to calculate the transpose of the cofactor matrix. It takes the form

$$B={}^t(\text{cofact } A)=\begin{bmatrix} b_{1111} & 0 & 0 & b_{1122} \\ 0 & b_{1212} & 0 & 0 \\ 0 & 0 & b_{2121} & 0 \\ 0 & 0 & 0 & b_{2222} \end{bmatrix} , \tag{3.21}$$

where

$$b_{1111}=(p-p_2)(p-p_3)(p-p_4)(p-p_5)/(p+\Gamma_{s\,vvvv}) ,$$

$$b_{1212}=p(p-p_3)(p-p_4)(p-p_5)/(p+\Gamma_{s\,vvvv}) ,$$

$$b_{2121}=p(p-p_2)(p-p_4)(p-p_5)/(p+\Gamma_{s\,vvvv}) .$$

$$b_{2222}=p(p-p_2)(p-p_3) ,$$

$$b_{1122}=-\Gamma_{11\,22}(p-p_2)(p-p_3) .$$

With the previous results, it is quite easy to obtain the various matrix elements of $G(p,0)$. To this end, we just need the explicit form of the matrix elements, given either by (3.19) in $\mathcal{P}$ or by (3.20) in Q, which will be identified with the definition (3.18). Therefore, we finally get matrix elements of the type

$$\tilde{G}_{ijkl}(p,0)=\frac{B_{ijkl}}{\prod_{i=1}^{5}(p-p_i)}(p+\Gamma_{s\,vvvv}) \quad \text{for } \mathcal{P}\text{-}\mathcal{P} \; ; \tag{3.22}$$

$$\tilde{G}_{ij\alpha\beta}(p,0)=-\sum_{k,l}\tilde{G}_{ijkl}(p,0)(\Gamma_{s\,kl\,\alpha\beta}+\Gamma_{kl\,\alpha\beta})\frac{1}{p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}} \quad \text{for } \mathcal{P}\text{-}Q \; ; \tag{3.23}$$

$$\tilde{G}_{\alpha\beta kl}(p,0)=-\frac{1}{p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}\sum_{i,j}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})\tilde{G}_{ijkl}(p,0) \quad \text{for } Q\text{-}\mathcal{P}\ ; \tag{3.24}$$

$$\tilde{G}_{\alpha\beta\lambda\mu}(p,0)=\frac{1}{p+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}} \times\left[\delta_{\alpha\lambda}\delta_{\beta\mu}+\sum_{i,j,k,l}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})\tilde{G}_{ijkl}(p,0)(\Gamma_{s\,kl\lambda\mu}+\Gamma_{kl\lambda\mu})\frac{1}{p+i\omega_{\lambda\mu}+\Gamma_{s\,\lambda\mu\lambda\mu}+\Gamma_{\lambda\mu\lambda\mu}}\right] \quad \text{for } Q\text{-}Q\ . \tag{3.25}$$

These quantities will enable us to explicitly set down the dynamics of a system undergoing a stochastic configuration interaction as well as pure dephasing processes.

IV. RELAXATION OF THE SYSTEM AND ABSORPTION SPECTRA

In Sec. III we calculated the functions $\tilde{G}(p,0)$ which drive the evolution of the free system. From the Laplace transform of these functions the evaluation of the one-photon absorption probability is straightforwardly carried out and the absorption spectra is deduced.

For this purpose, we introduce the Liouville equation of the total density matrix σ:

$$\frac{\partial\sigma}{\partial t}=-\frac{i}{\hbar}(L_s+R_s)\sigma-\Gamma\sigma-\frac{i}{\hbar}(L_F+L')\sigma \tag{4.1}$$

which includes, besides the Liouvillian of the free system previously described, the one of the field defined by

$$L_F=[\hbar\omega_k a_k^\dagger a_k,\ ] \tag{4.2}$$

and the one which accounts for the field-system interaction

$$L'=i\gamma[a_k|2\rangle\langle 1|-a_k^\dagger|1\rangle\langle 2|,\ ]\ . \tag{4.3}$$

In the previous expressions, a_k and $a_k^\dagger$ stand for the annihilation and creation photon operator in the k mode. In addition, for a one-photon process, the main contribution to the perturbation expansion of the density matrix will be given by the second-order term. Therefore, if $G(t,\tau)$ describes the free evolution of the system alone from the initial time τ to the final time t, a perturbation expansion with respect to L' can be performed.

In the present case, the second-order contribution to the total density matrix will be expressed by

$$\sigma^{(2)}(t)=-\frac{1}{\hbar^2}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2 G(t,\tau_1)e^{-(i/\hbar)L_F(t-\tau_1)}L'G(\tau_1,\tau_2)e^{-(i/\hbar)L_F(\tau_1-\tau_2)}L'G(\tau_2,0)e^{-(i/\hbar)L_F\tau_2}\sigma(0)\ . \tag{4.4}$$

If we assume at the initial time $t=0$ the material system in the ground state $|1\rangle$ and n photons present in the k mode of the radiation field, then

$$\sigma(0)=|1\rangle\langle 1|\otimes|n\rangle\langle n|\ . \tag{4.5}$$

The evaluation of (4.4) can now be done if the inverse Laplace transforms of the $\tilde{G}(p,0)$ matrix elements are known. Their expressions depend on the nature of the kets introduced. The various types of matrix elements are the following:

$$G_{ijkl}(t,0)=\sum_u e^{p_u t}\mathcal{R}(p_u) \quad \text{for } \mathcal{P}\text{-}\mathcal{P}\ , \tag{4.6}$$

where the quantity $\mathcal{R}(p_u)$ stands for the residue at the pole p_u of the function $B_{ijkl}(p)[\prod_{j=1}^{5}(p-p_i)]^{-1}$;

$$G_{ij\alpha\beta}(t,0)=-\sum_{u,k,l}e^{p_u t}\mathcal{R}(p_u)(\Gamma_{s\,kl\alpha\beta}+\Gamma_{kl\alpha\beta})\frac{1}{p_u+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}} -\sum_{k,l}\tilde{G}_{ijkl}(-i\omega_{\alpha\beta}-\Gamma_{s\,\alpha\beta\alpha\beta}-\Gamma_{\alpha\beta\alpha\beta},0)(\Gamma_{s\,kl\alpha\beta}+\Gamma_{kl\alpha\beta})e^{-(i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta})t} \quad \text{for } \mathcal{P}\text{-}Q\ ; \tag{4.7}$$

$$G_{\alpha\beta kl}(t,0)=\sum_u\frac{-1}{p_u+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}\sum_{i,j}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})e^{p_u t}\mathcal{R}(p_u) -e^{-(i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta})t}\sum_{i,j}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})\tilde{G}_{ijkl}(-i\omega_{\alpha\beta}-\Gamma_{s\,\alpha\beta\alpha\beta}-\Gamma_{\alpha\beta\alpha\beta},0) \quad \text{for } Q\text{-}\mathcal{P}\ ; \tag{4.8}$$

$$G_{\alpha\beta\lambda\mu}(t,0)=e^{-(i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta})t}$$
$$\times\left[\delta_{\alpha\beta}\delta_{\beta\mu}+\sum_{i,j,k,l}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})\tilde{G}_{ijkl}(-i\omega_{\alpha\beta}-\Gamma_{s\,\alpha\beta\alpha\beta}-\Gamma_{\alpha\beta\alpha\beta},0)(\Gamma_{s\,kl\lambda\mu}+\Gamma_{kl\lambda\mu})\right.$$
$$\left.\times\frac{1}{-i\omega_{\alpha\beta}-\Gamma_{s\,\alpha\beta\alpha\beta}-\Gamma_{\alpha\beta\alpha\beta}+i\omega_{\lambda\mu}+\Gamma_{s\,\lambda\mu\lambda\mu}+\Gamma_{\lambda\mu\lambda\mu}}\right]$$
$$+\sum_u\frac{1}{p_u+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}$$
$$\times\sum_{i,j,k,l}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})e^{p_u t}\mathcal{R}(p_u)(\Gamma_{s\,kl\lambda\mu}+\Gamma_{kl\lambda\mu})\frac{1}{p_u+i\omega_{\lambda\mu}+\Gamma_{s\,\lambda\mu\lambda\mu}+\Gamma_{\lambda\mu\lambda\mu}}$$
$$+\frac{1}{-i\omega_{\lambda\mu}-\Gamma_{s\,\lambda\mu\lambda\mu}-\Gamma_{\lambda\mu\lambda\mu}+i\omega_{\alpha\beta}+\Gamma_{s\,\alpha\beta\alpha\beta}+\Gamma_{\alpha\beta\alpha\beta}}$$
$$\times\sum_{i,j,k,l}(\Gamma_{s\,\alpha\beta ij}+\Gamma_{\alpha\beta ij})\tilde{G}_{ijkl}(-i\omega_{\lambda\mu}-\Gamma_{s\,\lambda\mu\lambda\mu}-\Gamma_{\lambda\mu\lambda\mu},0)$$
$$\times(\Gamma_{s\,kl\lambda\mu}+\Gamma_{kl\lambda\mu})e^{-(i\omega_{\lambda\mu}+\Gamma_{s\,\lambda\mu\lambda\mu}+\Gamma_{\lambda\mu\lambda\mu})t}\quad\text{for } Q\text{-}Q\ . \tag{4.9}$$

At this stage of the calculation, we really need to know what are the matrix elements of $G(t,0)$ which participate in the evaluation of the total density matrix $\sigma^{(2)}(t)$. Taking into account the simplifying assumptions previously introduced, the only nonzero matrix elements of Γ will be $(\Gamma_{22\,22},\Gamma_{11\,22},\Gamma_{12\,12},\Gamma_{2v\,2v},\Gamma_{vv'vv'})$ and those that can be deduced by symmetry rules. Similarly, for the stochastic operator, only the matrix elements $(\Gamma_{s\,22\,22},\Gamma_{s\,2v\,2v},\Gamma_{s\,22\,vv},\Gamma_{s\,vv\,vv})$ will be required, all the others being neglected. Consequently, the nonvanishing matrix elements of the Liouville operator will be

$$G_{1111},G_{1212},G_{2121},G_{1122}\quad\text{for } \mathcal{P}\text{-}\mathcal{P}\ ;$$
$$G_{11\alpha\alpha},G_{22\alpha\alpha}\quad\text{for } \mathcal{P}\text{-}Q\ ;$$
$$G_{\alpha\alpha22}\quad\text{for } Q\text{-}\mathcal{P}\ ;$$
$$G_{\alpha\beta\alpha\beta},G_{\alpha\alpha\beta\beta}\quad\text{for } Q\text{-}Q\ .$$

From the previous observations, we get the matrix elements of $\sigma^{(2)}(t)$ in the form

$$\langle 2,n-1|\sigma^{(2)}(t)|2,n-1\rangle=\frac{|H'_{21}|^2}{\hbar^2}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2 G_{2222}(t,\tau_1)[G_{1212}(\tau_1,\tau_2)e^{-i\omega(\tau_1-\tau_2)}+G_{2121}(\tau_1,\tau_2)e^{i\omega(\tau_1-\tau_2)}]\ ,$$
$$\langle v,n-1|\sigma^{(2)}(t)|v,n-1\rangle=\frac{|H'_{21}|^2}{\hbar^2}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2 G_{vv22}(t,\tau_1)[G_{1212}(\tau_1,\tau_2)e^{-i\omega(\tau_1-\tau_2)}+G_{2121}(\tau_1,\tau_2)e^{i\omega(\tau_1-\tau_2)}]\ , \tag{4.10}$$

where the notation $H'_{21}=\langle 2,n-1|H'|1,n\rangle$ has been introduced. The role of the isoenergetic manifold of states of the lower electronic configuration consists in a supplementary contribution to the one-photon absorption probability given by the second term in relation (4.10). If we evaluate the different factors participating to the integrals, one successively obtains

$$G_{2222}(t,\tau_1)[G_{1212}(\tau_1,\tau_2)e^{-i\omega(\tau_1-\tau_2)}+G_{2121}(\tau_1,\tau_2)e^{i\omega(\tau_1-\tau_2)}]=\frac{1}{p_4-p_5}[(p_4+\Gamma_{s\,vvvv})e^{p_4(t-\tau_1)}-(p_5+\Gamma_{s\,vvvv})e^{p_5(t-\tau_1)}]$$
$$\times(e^{(p_2-i\omega)(\tau_1-\tau_2)}+e^{(p_3+i\omega)(\tau_1-\tau_2)})\ ,$$
$$G_{vv22}(t,\tau_1)[G_{1212}(\tau_1,\tau_2)e^{-i\omega(\tau_1-\tau_2)}+G_{2121}(\tau_1,\tau_2)e^{i\omega(\tau_1-\tau_2)}]=-\left[\frac{\Gamma_{s\,vv\,22}}{(p_4-p_5)}e^{p_4(t-\tau_1)}+\frac{\Gamma_{s\,vv\,22}}{(p_5-p_4)}e^{p_5(t-\tau_1)}\right]$$
$$\times(e^{(p_2-i\omega)(\tau_1-\tau_2)}+e^{(p_3+i\omega)(\tau_1-\tau_2)})\ . \tag{4.11}$$

Therefore, we are now able to determine the transition probability for a single-photon absorption process. It takes the form

$$P(t)=\langle 2,n-1|\sigma^{(2)}(t)|2,n-1\rangle+\sum_{v}\langle v,n-1|\sigma^{(2)}(t)|v,n-1\rangle \ . \tag{4.12}$$

If we note that all the contributions can be expressed as

$$Ae^{\Lambda t}\int_0^t d\tau_1\int_0^{\tau_1} d\tau_2 e^{\alpha\tau_1+\beta\tau_2}=\frac{A}{\beta(\alpha+\beta)}(e^{(\alpha+\beta+\Lambda)t}-e^{\Lambda t})-\frac{A}{\beta\alpha}(e^{(\alpha+\Lambda)t}-e^{\Lambda t}) \ , \tag{4.13}$$

the probability is finally given by the expression

$$P(t)=\frac{|H'_{21}|^2}{\hbar^2}\left[\sum_{i=1}^{4}\left[\frac{A_i}{\beta_i(\alpha_i+\beta_i)}(1-e^{\Lambda_i t})-\frac{A_i}{\beta_i\alpha_i}(e^{(\alpha_i+\Lambda_i)t}-e^{\Lambda_i t})\right]\right.$$
$$\left.+\sum_{i=1}^{4}\left[\frac{NB_i}{\lambda_i(\nu_i+\lambda_i)}(1-e^{\Delta_i t})-\frac{NB_i}{\lambda_i\nu_i}(e^{(\nu_i+\Delta_i)t}-e^{\Delta_i t})\right]\right] \tag{4.14}$$

if we keep in mind that all the states $|v\rangle$ play the same role because of our previous assumptions. The first term describes the dynamics of the state $|2\rangle$ as if it were alone and the second term describes how they are altered by the isoenergetic configuration. They will be written as $P_2(t)$ and $P_v(t)$, respectively. Also, we have introduced the notation

i	α_i	Λ_i	A_i	ν_i	Δ_i	B_i
1	$p_2-p_4-i\omega$	p_4	$\dfrac{p_4+\Gamma_{s\,vv\,vv}}{p_4-p_5}$	α_1	Λ_1	$\dfrac{-\Gamma_{s\,vv\,22}}{p_4-p_5}$
2	$p_3-p_4+i\omega$	p_4	A_1	α_2	Λ_2	B_1
3	$p_2-p_5-i\omega$	p_5	$\dfrac{p_5+\Gamma_{s\,vv\,vv}}{p_5-p_4}$	α_3	Λ_3	$-B_1$
4	$p_3-p_5+i\omega$	p_5	A_3	α_4	Λ_4	$-B_1$

where

$$\alpha_i+\beta_i+\Lambda_i=\nu_i+\lambda_i+\Delta_i=0 \quad \forall i \ .$$

Section V will be devoted to a physical discussion of the probability $P(t)$.

V. NUMERICAL CALCULATIONS AND DISCUSSIONS

We have carried out some numerical calculations from the analytical expression of the one-photon absorption process given by relation (4.14). They will be helpful in discussing the influence of the various physical parameters such as dephasing and transition rate constants or the number of nonradiant states. Also, it will be of interest to note that for each separate set of figures, tick marks indicate the relative scale.

The general shape of the variations of $P(t)$ is represented in Fig. 2. For a system initially unexcited, these variations show a monotonic increase with time with a zero derivative at the initial time $t=0$ and an asymptotic constant limit for long times. This observation is still true for both contributions previously discussed, that is to say, the one corresponding to the population of state $|2\rangle$ and those generated by the population of the nonradiant states $|v\rangle$. Nevertheless, the second contribution increases more slowly than the first one at short times. This is because states $|v\rangle$ can only be populated from state $|2\rangle$. If the configuration interaction couples only one nonradiant state to $|2\rangle$, the asymptotic values would be the same as shown on Fig. 2. In addition, this result is independent of the relative values of the transition rates Γ_{1122} and $\Gamma_{s\,vv22}$. Taking into account the behavior of $P(t)$ in the long-time limit, a discussion of the results presented in Fig. 3 can be given. Here, we have analyzed the separate variations of $P_2(t)$ and $P_v(t)$ like those of the total one-photon absorption probability $P(t)$ for different values of $\Gamma_{s\,vv22}$. At short times, the second contribution [Fig. 3(b)] increases more slowly for small but nonzero values of $\Gamma_{s\,vv22}$ than for higher values. However, the reverse situation is observed at long times. The first contribution reaches its asymptotic limit on a time scale defined by Γ_{1122}, that is to say, more rapidly than the second one. Finally, when $\Gamma_{s\,vv22}$ becomes negligible, a situation which corresponds to a two-level system with no stochastic interaction, $P_v(t)$ will start to increase for infinitely long times, so that only the first contribution will subsist. Of course, this result can also be established from the analytical expression (4.14) because in this limit, the pole p_5 will be zero. In Fig. 4, it is shown that if $\Gamma_{1122}\ll\Gamma_{s\,vv22}$ both contributions have similar behavior. This is because Γ_{1122} defines the time scale on which the excited state can be populated taking into account that nonradiant states can only be populated from state $|2\rangle$.

In addition, it is quite interesting to study the time dependence of the total probability with N, the number of nonradiant states. The first observation can be done on Fig. 5 concerning $P_2(t)$ and $P_v(t)$, respectively. In these figures, we introduce simultaneously the variations of N and $\Gamma_{s\,vv22}$ by keeping the product $N\Gamma_{s\,vv22}$ constant. This is purposefully done to have the same total lifetime for the excited state $|2\rangle$ in both cases. We note an increase of $P(t)$ approximately linear with N, while $P_2(t)$ is only weakly modified by these parameters. This comes from the dominant population effect on the $|v\rangle$ states, the population retention being more efficient when the number of $|v\rangle$ states is large, even at the expense of the transition rates $\Gamma_{s\,vv22}$. On the contrary, if we introduce a change of N keeping $\Gamma_{s\,vv22}$ constant, we obtain the results shown in Figs. 6 and 7. In the first figures, we note that the increase in the number of levels is obtained at the expense of the total lifetime of the radiant state and consequently at the expense of $P_2(t)$. On the other hand, this variation is done for the benefit of the second contribution. Therefore, the total one-photon absorption probability will exhibit the first or the second type of behavior

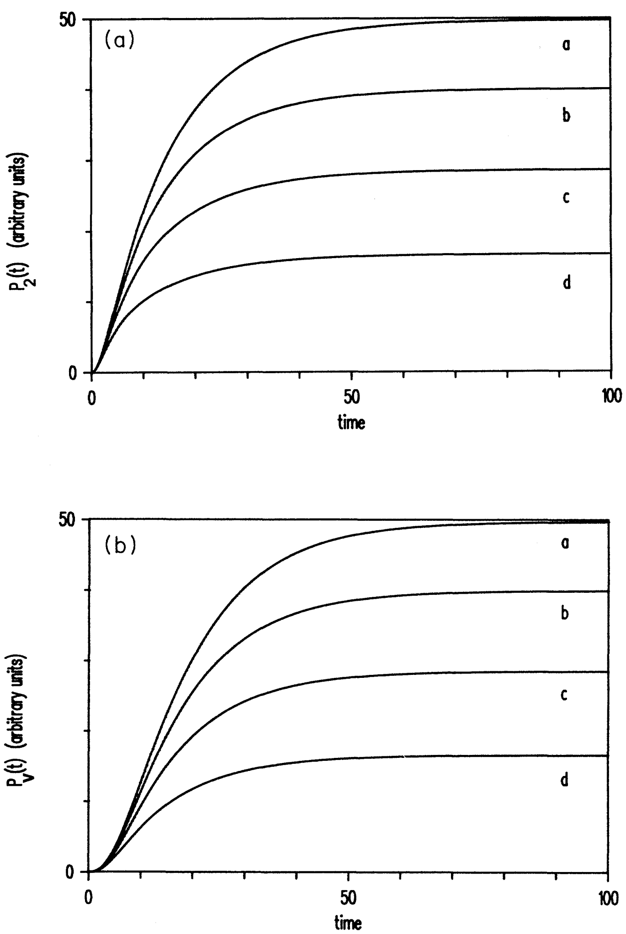

FIG. 2. Time dependence of the contributions (a) $P_2(t)$ and (b) $P_v(t)$ for different values of the pure dephasing constants $\Gamma_{12}^{(d)}$ equal to (a) 0, (b) 0.05, (c) 0.15, (d) 0.4. The other parameters are $\omega_{21}=\omega=10$, $\Gamma_{1122}=-0.2$, $\Gamma_{s\,vv22}=-0.2$, $N=1$. The same scale has been chosen for the vertical axis.

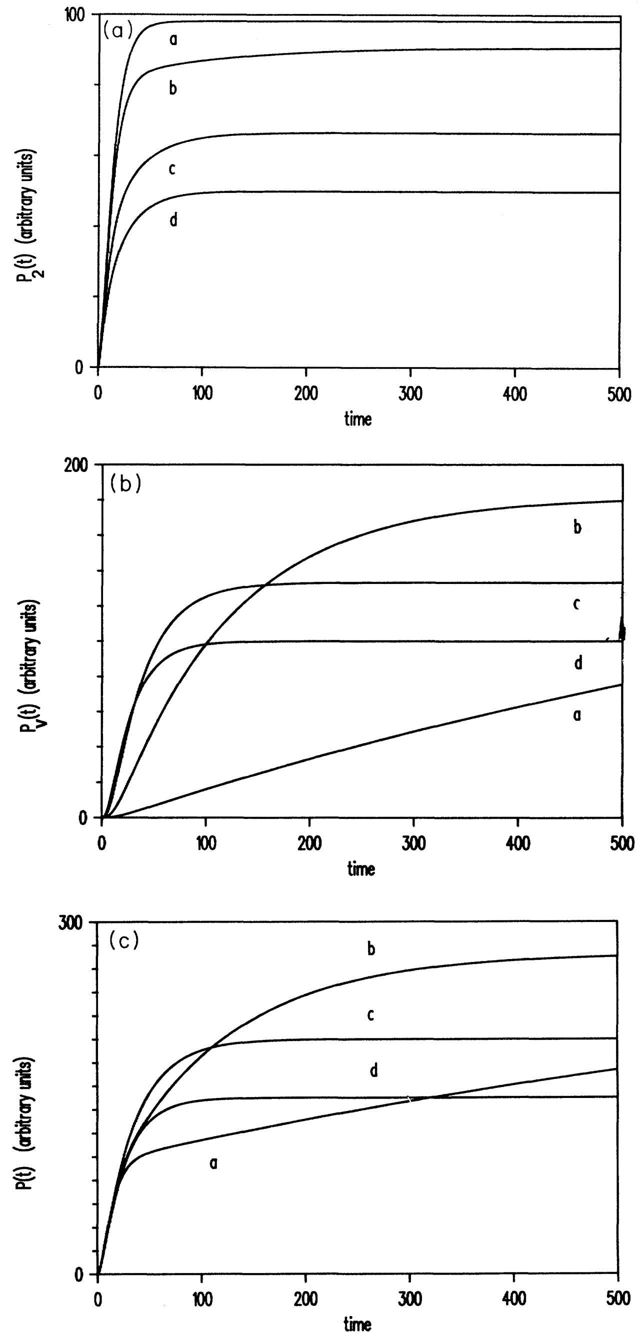

FIG. 3. Time dependence of the contributions (a) $P_2(t)$ and (b) $P_v(t)$ to the absorption probability (c) $P(t)$ for different values of the stochastic transition constant: $\Gamma_{s\,vv22}$ equal to (a) 0.001, (b) 0.01, (c) 0.05, (d) 0.1. The other parameters are given by $\omega_{21}=\omega=10$, $\Gamma_{1122}=-0.2$, $\Gamma_{12}^{(d)}=0$, $N=2$.

depending on the relative values $\Gamma_{s\,vv22} > \Gamma_{1122}$ [Fig. 7(c)] or $\Gamma_{s\,vv22} < \Gamma_{1122}$ [Fig. 7(a)]. In the particular case $\Gamma_{s\,vv22} = \Gamma_{1122}$ both variations will compensate exactly and the value of $P(t=\infty)$ is independent of N [Fig. 7(b)].

Finally, we show the absorption spectrum, that is to say, the variation of $P(t=\infty)$ as a function of the excitation field frequency. Fig. 8 exhibits a quasi-Lorentzian type of behavior and this is still true for both contributions $P_2(t=\infty)$ and $P_v(t=\infty)$. In addition, the ratio between the second and the first contribution is equal to N, the number of coupled states. Therefore, here again, we note the dominant role of the populations.

VI. CONCLUSION

In this paper, we took advantage of a general formalism initially introduced by Faid and Fox, and later extended by ourselves to more complex systems, to study the internal dynamics of material systems. While former works were dedicated to the description of a stochastic theory of the relaxation, we have emphasized more the influence of the stochastic couplings on the internal dynamics. In the present study, the final thermalization of the system is generated by a heat bath and is completely independent of the stochastic interactions acting in the excited states only. Our description is valid for diagonal and nondiagonal interactions. Also, dephasing processes have been introduced in the model. This point is of particular interest since the important role by coherence effects in nonradiative decay has been demonstrated recently [30]. Only the Markovian and the weakly colored noise cases have been studied. The extension of our descriptions to non-δ-correlated stochastic processes, similar to the slow fluctuation limit case of modulation frequency, cannot be handled in this way. Because of the time dependence of the autocorrelation function of the stochastic variables, a specific evaluation of the model is

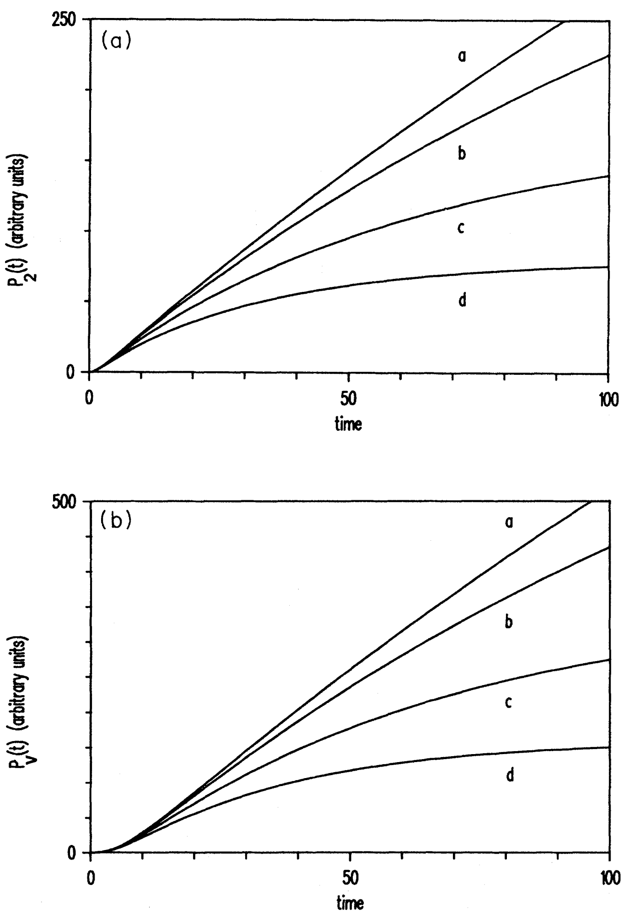

FIG. 4. Influence of the transition constant Γ_{1122} on the time dependence of the contributions (a) $P_2(t)$ and (b) $P_v(t)$ to the total absorption probability. Different values are considered: Γ_{1122} equal to (a) -0.01, (b) -0.02, (c) -0.05, (d) -0.1. The other parameters are $\omega_{21}=\omega=10$, $\Gamma_{12}^{(d)}=0$, $\Gamma_{s\,vv22}=-0.2$, $N=2$.

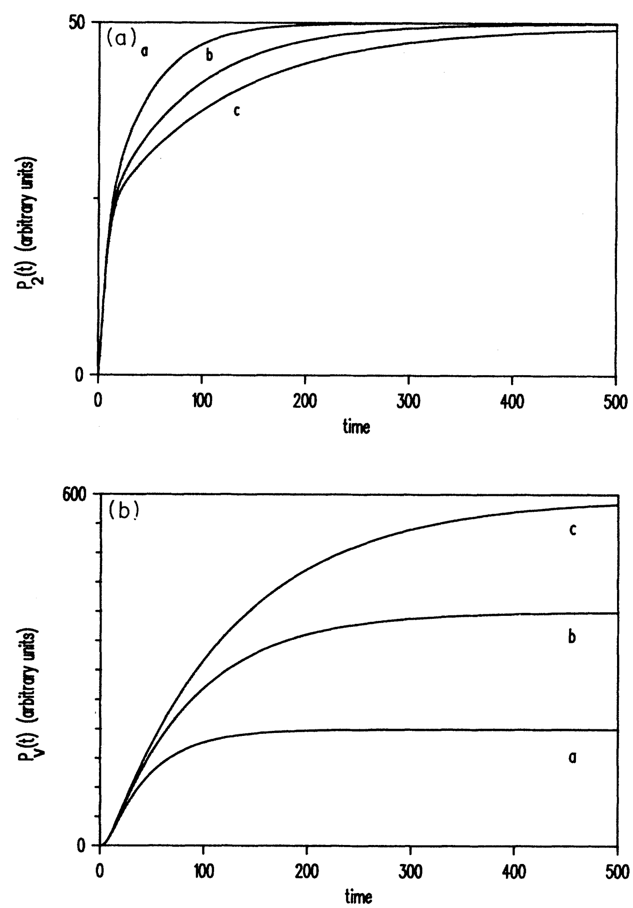

FIG. 5. We sketch the time dependence of (a) $P_v(t)$ and (b) $P_2(t)$ for different numbers of nonradiant states, but keeping the product $N\Gamma_{s\,vv22}$ constant: N equal to (a) 4, (b) 8, (c) 12. The other parameters are $\omega_{21}=\omega=10$, $\Gamma_{1122}=-0.2$, $\Gamma_{12}^{(d)}=0$, $N\Gamma_{s\,vv22}=-0.2$.

required. In fact, no general mathematical methods are available to extend these studies to more complex systems in this limit. Moreover, up to now, there has been no treatment of the frequency modulation that included pure dephasing, even for simple systems.

Two different applications have been presented here. In the first one the dynamics of a three-level system has been described. This model is relevant for explaining the solvent effects on resonance Raman scattering and luminescence of the β-carotene molecule in the motional narrowing limit [31]. Here, electronic and vibrational dephasing can be introduced straightforwardly. The second application is devoted to the stochastic configuration interaction. This study can serve as a model for systems undergoing nonradiative transitions induced by a stochastic coupling. Here, the one-photon absorption process has been evaluated and the contributions corresponding to the excited state and to the manifold of nonradiant states have been analyzed separately. Finally, the influence of the decay and transition rate constants as well as that of the number of nonradiant states have been discussed.

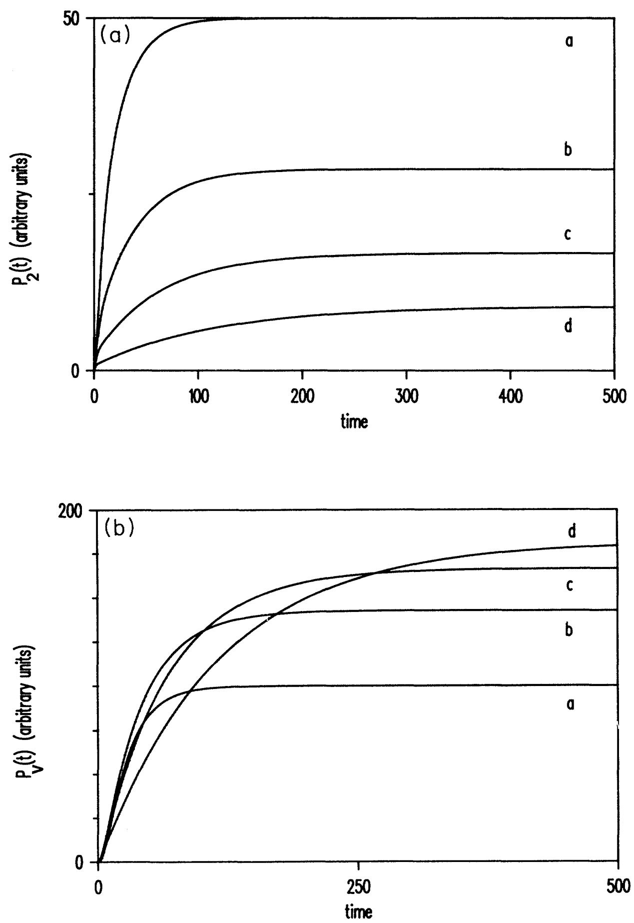

FIG. 6. Same variations as in Fig. 5 except that here $\Gamma_{s\,vv22}=-0.1$. The values of N are (a) 2, (b) 5, (c) 10, (d) 20 and the other parameters are kept the same.

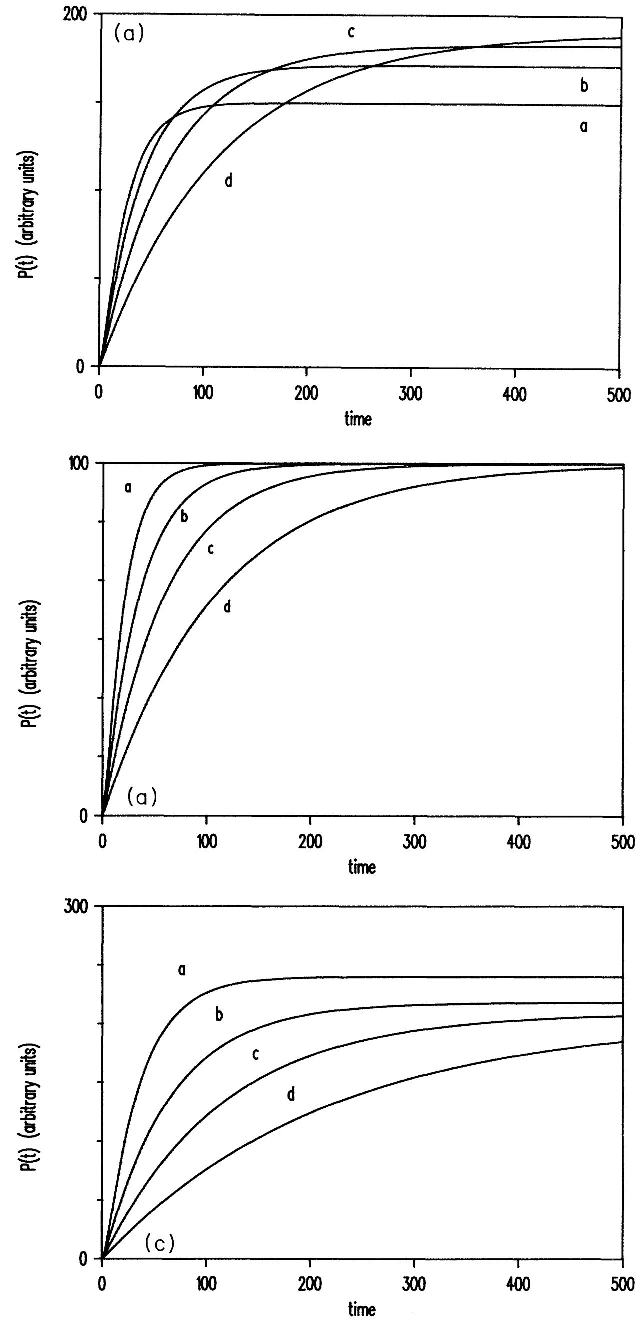

FIG. 7. Time dependence of the total transition probability $P(t)$ for different numbers of nonradiant states: N equal to (a) 2, (b) 5, (c) 10, (d) 20. The other parameters are $\omega_{21}=\omega=10$, $\Gamma_{12}^{(d)}=0$. The various figures correspond to (a) $\Gamma_{1122}=-0.2$, $\Gamma_{s\,vv22}=-0.1$; (b) $\Gamma_{1122}=-0.2$, $\Gamma_{s\,vv22}=-0.2$; (c) $\Gamma_{1122}=-0.1$, $\Gamma_{s\,vv22}=-0.2$.

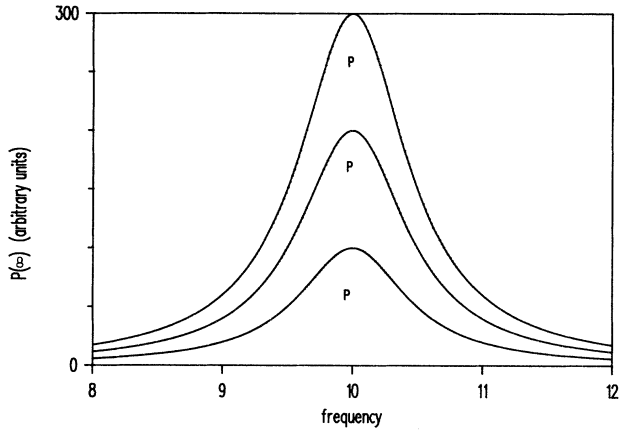

FIG. 8. Frequency dependence of the absorption spectrum $P(t=\infty)$. The parameters are $\omega_{21}=10$, $\Gamma_{1122}=-0.2$, $\Gamma^{(d)}_{12}=0.2$, $\Gamma_{s\,vv22}=-0.2$, $N=2$.

APPENDIX A

We give here the matrices corresponding to the SU(3) generators:

$$I_1=\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix},\quad I_2=\begin{bmatrix}0&-i&0\\i&0&0\\0&0&0\end{bmatrix},$$

$$I_3=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&0\end{bmatrix},\quad I_4=\begin{bmatrix}0&0&1\\0&0&0\\1&0&0\end{bmatrix},$$

$$I_5=\begin{bmatrix}0&0&-i\\0&0&0\\i&0&0\end{bmatrix},\quad I_6=\begin{bmatrix}0&0&0\\0&0&1\\0&1&0\end{bmatrix},$$

$$I_7=\begin{bmatrix}0&0&0\\0&0&-i\\0&i&0\end{bmatrix},\quad I_8=\frac{1}{\sqrt{3}}\begin{bmatrix}1&0&0\\0&1&0\\0&0&-2\end{bmatrix}.$$

APPENDIX B

$$K_{11}=\tfrac{1}{2}(\Gamma_{s\,2121}+\Gamma_{s\,1212}+\Gamma_{s\,2112}+\Gamma_{s\,1221}+\Gamma_{2121}+\Gamma_{1212}),$$

$$K_{21}=\frac{i}{2}(2i\omega_{21}+\Gamma_{s\,2121}-\Gamma_{s\,1212}-\Gamma_{s\,2112}+\Gamma_{s\,1221}+\Gamma_{2121}-\Gamma_{1212}),$$

$$K_{21}=-\frac{i}{2}(2i\omega_{21}+\Gamma_{s\,2121}-\Gamma_{s\,1212}+\Gamma_{s\,2112}-\Gamma_{s\,1221}+\Gamma_{2121}-\Gamma_{1212}),$$

$$K_{22}=\tfrac{1}{2}(\Gamma_{s\,2121}+\Gamma_{s\,1212}-\Gamma_{s\,2112}-\Gamma_{s\,1221}+\Gamma_{2121}+\Gamma_{1212}),$$

$$K_{33}=\tfrac{1}{2}(\Gamma_{s\,1111}-\Gamma_{s\,1122}-\Gamma_{s\,2211}+\Gamma_{s\,2222}+\Gamma_{1111}-\Gamma_{1122}-\Gamma_{2211}+\Gamma_{2222}),$$

$$K_{38}=\frac{1}{2\sqrt{3}}(\Gamma_{s\,1111}+\Gamma_{s\,1122}-2\Gamma_{s\,1133}-\Gamma_{s\,2211}-\Gamma_{s\,2222}+2\Gamma_{s\,2233}+\Gamma_{1111}+\Gamma_{1122}-2\Gamma_{1133}-\Gamma_{2211}-\Gamma_{2222}+2\Gamma_{2233}),$$

$$K_{30}=\tfrac{1}{6}(\Gamma_{1111}+\Gamma_{1122}+\Gamma_{1133}-\Gamma_{2211}-\Gamma_{2222}-\Gamma_{2233}),$$

$$K_{83}=\frac{1}{2\sqrt{3}}(\Gamma_{s\,1111}-\Gamma_{s\,1122}+\Gamma_{s\,2211}-\Gamma_{s\,2222}-2\Gamma_{s\,3311}+2\Gamma_{s\,3322}$$
$$+\Gamma_{1111}-\Gamma_{1122}+\Gamma_{2211}-\Gamma_{2222}-2\Gamma_{3311}+2\Gamma_{3322}),$$

$$K_{88}=\tfrac{1}{6}(\Gamma_{s\,1111}+\Gamma_{s\,1122}-2\Gamma_{s\,1133}+\Gamma_{s\,2211}+\Gamma_{s\,2222}-2\Gamma_{s\,2233}-2\Gamma_{s\,3311}-2\Gamma_{s\,3322}+4\Gamma_{s\,3333}+\Gamma_{1111}+\Gamma_{1122}-2\Gamma_{1133}$$
$$+\Gamma_{2211}+\Gamma_{2222}-2\Gamma_{2233}-2\Gamma_{3311}-2\Gamma_{3322}+4\Gamma_{3333}),$$

$$K_{80}=\frac{1}{6\sqrt{3}}(\Gamma_{1111}+\Gamma_{1122}+\Gamma_{1133}+\Gamma_{2211}+\Gamma_{2222}+\Gamma_{2233}-2\Gamma_{3311}-2\Gamma_{3322}-2\Gamma_{3333}),$$

$$K_{44}=\tfrac{1}{2}(\Gamma_{s\,3131}+\Gamma_{s\,1313}+\Gamma_{s\,3113}+\Gamma_{s\,1331}+\Gamma_{3131}+\Gamma_{1313}),$$

$$K_{45}=\frac{i}{2}(2i\omega_{31}+\Gamma_{s\,3131}-\Gamma_{s\,1313}-\Gamma_{s\,3113}+\Gamma_{s\,1331}+\Gamma_{3131}-\Gamma_{1313}),$$

$$K_{54}=-\frac{i}{2}(2i\omega_{31}+\Gamma_{s\,3131}-\Gamma_{s\,1313}+\Gamma_{s\,3113}-\Gamma_{s\,1331}+\Gamma_{3131}-\Gamma_{1313}),$$

$$K_{55}=\tfrac{1}{2}(\Gamma_{s\,3131}+\Gamma_{s\,1313}-\Gamma_{s\,3113}-\Gamma_{s\,1331}+\Gamma_{3131}+\Gamma_{1313}),$$

$$K_{66}=\tfrac{1}{2}(\Gamma_{s\,3232}+\Gamma_{s\,2323}+\Gamma_{s\,3223}+\Gamma_{s\,2332}+\Gamma_{3232}+\Gamma_{2323}),$$

$$K_{67}=\frac{i}{2}(2i\omega_{32}+\Gamma_{s\,3232}-\Gamma_{s\,2323}-\Gamma_{s\,3223}+\Gamma_{s\,2332}+\Gamma_{3232}-\Gamma_{2323}),$$

$$K_{76}=-\frac{i}{2}(2i\omega_{32}+\Gamma_{s\,3232}-\Gamma_{s\,2323}+\Gamma_{s\,3223}-\Gamma_{s\,2332}+\Gamma_{3232}-\Gamma_{2323})\ ,$$

$$K_{77}=\tfrac{1}{2}(\Gamma_{s\,3232}+\Gamma_{s\,2323}-\Gamma_{s\,3223}-\Gamma_{s\,2332}+\Gamma_{3232}+\Gamma_{2323})\ .$$

APPENDIX C

We report the explicit expressions of the $G_{ijkl}(t,0)$ matrix elements required to describe any time evolution of a stochastic three-level system in the Markovian or the weakly colored noise cases:

$$\begin{aligned}
G_{1111}(t,0)=\tfrac{1}{3}+M_{30}+\frac{1}{\sqrt{3}}M_{80}&+\frac{e^{\lambda_{38}^{\dagger}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{30}(\lambda_{38}^{+}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]\\
&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{30}(\lambda_{38}^{-}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]\\
&+\frac{1}{2}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[\lambda_{38}^{+}(\lambda_{38}^{+}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{+}\right]+\frac{1}{2}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[\lambda_{38}^{-}(\lambda_{38}^{-}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{-}\right]\\
&+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]\\
&+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right]\ ,
\end{aligned}$$

$$\begin{aligned}
G_{1122}(t,0)=\tfrac{1}{3}+M_{30}+\frac{1}{\sqrt{3}}M_{80}&+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{30}(\lambda_{38}^{+}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]\\
&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{30}(\lambda_{38}^{-}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]\\
&-\frac{1}{2}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[\lambda_{38}^{+}(\lambda_{38}^{+}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{+}\right]-\frac{1}{2}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[\lambda_{38}^{-}(\lambda_{38}^{-}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{-}\right]\\
&+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]\\
&+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right]\ ,
\end{aligned}$$

$$\begin{aligned}
G_{1133}(t,0)=\tfrac{1}{3}+M_{30}+\frac{1}{\sqrt{3}}M_{80}&+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{30}(\lambda_{38}^{+}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]\\
&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{30}(\lambda_{38}^{-}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]\\
&-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]\\
&-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right]\ ,
\end{aligned}$$

$$\begin{aligned}
G_{2211}(t,0)=\tfrac{1}{3}-M_{30}+\frac{1}{\sqrt{3}}M_{80}&+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{30}(\lambda_{38}^{+}+K_{88})-K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]\\
&+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{30}(\lambda_{38}^{-}+K_{88})-K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]
\end{aligned}$$

$$+\frac{1}{2}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-\lambda_{38}^{+}(\lambda_{38}^{+}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{+}\right]+\frac{1}{2}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-\lambda_{38}^{-}(\lambda_{38}^{-}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{-}\right]$$

$$+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right],$$

$$G_{2222}(t,0)=\tfrac{1}{3}-M_{30}+\frac{1}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{30}(\lambda_{38}^{+}+K_{88})-K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80})\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]$$

$$+\frac{e_{38}^{-}t}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{30}(\lambda_{38}^{-}+K_{88})-K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}K_{33})+K_{83}K_{30}]\right]$$

$$-\frac{1}{2}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[-\lambda_{38}^{+}(\lambda_{38}^{+}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{+}\right]-\frac{1}{2}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[-\lambda_{38}^{-}(\lambda_{38}^{-}+K_{88})-\frac{1}{\sqrt{3}}K_{83}\lambda_{38}^{-}\right]$$

$$+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]+\frac{\sqrt{3}}{6}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right],$$

$$G_{2233}(t,0)=\tfrac{1}{3}-M_{30}+\frac{1}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{30}(\lambda_{38}^{+}+K_{88})-K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{+}+K_{33})+K_{83}K_{30}]\right]$$

$$+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{30}(\lambda_{38}^{-}+K_{88})+K_{38}K_{80}+\frac{1}{\sqrt{3}}[-K_{80}(\lambda_{38}^{-}+K_{33})+K_{83}K_{30}]\right]$$

$$-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\left[K_{38}\lambda_{38}^{+}+\frac{1}{\sqrt{3}}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})\right]-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\left[K_{38}\lambda_{38}^{-}+\frac{1}{\sqrt{3}}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33})\right],$$

$$G_{3311}(t,0)=\frac{1}{3}-\frac{2}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{38}^{+}+K_{33})-K_{83}K_{30}]$$

$$+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{38}^{-}+K_{33})-K_{83}K_{30}]+\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}K_{83}\lambda_{38}^{+}$$

$$+\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}K_{83}\lambda_{38}^{-}-\frac{1}{3}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})-\frac{1}{3}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33}),$$

$$G_{3322}(t,0)=\frac{1}{3}-\frac{2}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{80}^{+}+K_{33})-K_{83}K_{30}]$$

$$+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{38}^{-}+K_{33})-K_{83}K_{30}]-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}K_{83}\lambda_{38}^{+}$$

$$-\frac{1}{\sqrt{3}}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}K_{83}\lambda_{38}^{-}-\frac{1}{3}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})-\frac{1}{3}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33}),$$

$$G_{3333}(t,0)=\frac{1}{3}-\frac{2}{\sqrt{3}}M_{80}+\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{38}^{+}+K_{33})-K_{83}K_{30}]$$

$$+\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\frac{2}{\sqrt{3}}[K_{80}(\lambda_{38}^{-}+K_{33})-K_{83}K_{30}]+\frac{2}{3}\frac{e^{\lambda_{38}^{+}t}}{\lambda_{38}^{+}(\lambda_{38}^{+}-\lambda_{38}^{-})}\lambda_{38}^{+}(\lambda_{38}^{+}+K_{33})$$

$$+\frac{2}{3}\frac{e^{\lambda_{38}^{-}t}}{\lambda_{38}^{-}(\lambda_{38}^{-}-\lambda_{38}^{+})}\lambda_{38}^{-}(\lambda_{38}^{-}+K_{33}).$$

All the other elements can be straightforwardly deduced from the expressions (2.20) and (2.22).

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