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Coherence-population interdependence in nonlinear optics

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Two-level systems are widely used in nonlinear optics; some authors have considered larger systems, but in most of these descriptions the additional levels participate in the dynamics of the two main levels through kinetic rate constants only. Here, we adopt a different point of view. Knowing that two-level models treated in a perturbational approach show peculiar relations between populations and coherences, we analyze the effect of a third perturbating level on these relations. An estimate of the extra contribution to the third-order coherence is made. The role of the dephasing processes on this contribution is analyzed.

I. INTRODUCTION

Nonlinear optical responses of molecular media are being extensively studied.[1] Most of these experiments, including decay as well as dephasing processes, have been successfully described by the optical Bloch equations.[2-5] While this theoretical framework is quite well adapted and has been used for a long time in other fields, it seems to us that the application of the oversimplified modelization to organic materials is often of questionable validity. Even in the cases where the main dynamical processes seem very well understood, it is essential to have at least a qualitative and, when possible, a quantitative estimate of how the environment could affect this simplified dynamical scheme. By environment we mean all what has been neglected in the model. This ranges from a simple perturbating level interacting with one of the excited states up to the more complex dissipative bath. A particular emphasis has been put recently on systems subjected to stochastic perturbations where the effect of the thermal bath can be described as a modulation of the electronic transition frequency.[6-8] Of course, such approaches cannot include large interactions.

While this last physical situation is of great interest and has been considered in a number of papers, we will be interested in this preliminary work by the opposite extreme case of a single perturbating level interacting with the excited state. Perhaps the strongest motivation for the present work is the tremendous emphasis put on two-level systems in nonlinear optical studies. In fact, formal solutions to optical Bloch equations for two-level models reveal a very peculiar structure which is not valid any more for many-level systems.[9] They decouple the contributions to populations and coherences and make them depend on the order of perturbation. For instance, the even orders give corrections to the populations only, while the odd orders contribute to the coherences only. In addition, contributions to a given order depended strictly on the contributions to the $(n-1)$th order. As a consequence, we have no direct population-population or coherence-coherence contribution when going from one order of perturbation to the next. It is clear that such relations result from the very peculiar properties of two-level systems. It is therefore tempting to analyze the influence of a third level, participating even weakly to the dynamics, on the nonlinear optical properties of the system.

The paper is organized as follows. In Sec. II, we present the perturbation method on which the present work is based. It includes the evaluation of the populations and coherences up to the third order for a general N-level system. When restricted to a two-level system, the results of Mitsunaga and Brewer[9] are recovered. However, when applied to larger systems, the third-order coherence contribution $\rho_{nm}^{(3)}(t)$ depends on the second-order populations $\rho_{nn}^{(2)}(t)$ as well as on the second-order coherences $\rho_{nm}^{(2)}(t)$. This extra contribution does not exist for a two-level system. Section III is devoted to the calculation of the corresponding optical susceptibilities. In Sec. IV we analyze the relations existing between populations and coherences and how they contribute to the various susceptibilities. We are then in a position to present and discuss the influence of a third perturbating level on the response of a two-level system undergoing a phase conjugation experiment. This is the purpose of Sec. V. Section VI will briefly draw some conclusions.

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II. PERTURBATION METHOD FOR POPULATIONS AND COHERENCES

In a previous paper devoted to the transient analysis of optical phase conjugation in two-level absorbing systems the perturbation method has been applied.[10,11] Here, we shall generalize the treatment to many-level systems. For this purpose, we write the Hamiltonian as

$$H=H_0+\lambda H'(t) , \tag{2.1}$$

where λ is the perturbation parameter and $H'(t)$ represents the interaction between the system and radiation fields and the residual interaction specific of the physical system. Of course, this last interaction is not time dependent, but for the sake of simplicity, we will include it. Distinction between both interactions will be introduced when necessary.

We start with the stochastic Liouville equation

$$\frac{d\rho}{dt}=-iL\rho-\Gamma\rho , \tag{2.2}$$

where Γ is the damping operator and L denotes the Liouville operator of the total system under the influence of radiation fields. That is, L can be separated into two parts; L_0 is the Liouville operator associated to some model system defined by H_0, while $L'(t)$ accounts for the interaction between the system and radiation fields as well as the internal residual interaction,

$$L=L_0+\lambda L'(t) . \tag{2.3}$$

In principle, the determination of $\rho(t)$ from Eq. (2.2) allows us to evaluate the polarization per unit molecule. It follows from the expression

$$\mathrm{p}=\mathrm{Tr}[\rho(t)\boldsymbol{\mu}] , \tag{2.4}$$

where $\boldsymbol{\mu}$ represents the dipole operator. In the following we shall apply the perturbation method to obtain $\rho_{nn}(t)$ and $\rho_{nm}(t)$ and a particular emphasis will be placed on the results for three-level systems.

From the expansion of $\rho(t)$ in power series of λ

$$\rho(t)=\rho^{(0)}(t)+\lambda\rho^{(1)}(t)+\lambda^2\rho^{(2)}(t)+\cdots \tag{2.5}$$

we deduce the various order approximations to Eq. (2.2). In the zeroth-order approximation, we have

$$\frac{d\rho^{(0)}}{dt}=-iL_0\rho^{(0)}-\Gamma\rho^{(0)} , \tag{2.6}$$

or, in terms of the diagonal and off-diagonal parts, with $\hbar\omega_{nm}=E_n-E_m$,

$$\begin{aligned}\frac{d\rho_{nn}^{(0)}}{dt}&=-\sum_m \Gamma_{n:m}\rho_{mm}^{(0)} ,\\ \frac{d\rho_{nm}^{(0)}}{dt}&=-(i\omega_{nm}+\Gamma_{nm})\rho_{nm}^{(0)} ,\end{aligned} \tag{2.7}$$

where the usual notation for the tetradic damping operator has been introduced,[12] i.e.,

$$\begin{aligned}\Gamma_{nn,mm}&=\Gamma_{n:m} ,\\ \Gamma_{nm}&=\tfrac{1}{2}(\Gamma_{n:n}+\Gamma_{m:m})+\Gamma_{nm}^{(d)} ,\end{aligned} \tag{2.8}$$

where $\Gamma_{n:n}$ is the total decay rate of level n, $\Gamma_{n:m}$ the transition rate of the $n\leftarrow m$ transition, and $\Gamma_{nm}^{(d)}$ the pure dephasing constant. Solutions to these master equations are straightforwardly obtained if the initial conditions are well defined. For the purpose of this work we will assume that at $t=0$ the system is in equilibrium. This means $\rho_{nn}(0)=\rho_{nn}^0$ as resulting, for example, from a Boltzmann population for the stationary states, $\rho_{nn}(0)=0$ for the nonstationary states and as usual $\rho_{nm}(0)=0$ because there is no initial correlation in the material system with these previous assumptions. The zeroth-order approximation gives the trivial result

$$\begin{aligned}&\rho_{nn}^{(0)}(t)=\rho_{nn}^{(0)} \text{ or } 0 ,\\ &\rho_{nm}^{(0)}(t)=0 .\end{aligned} \tag{2.9}$$

Next, we consider the first-order approximation. The dynamical equation takes the form

$$\frac{d\rho^{(1)}}{dt}=-iL_0\rho^{(1)}-iL'(t)\rho^{(0)}-\Gamma\rho^{(0)} \tag{2.10}$$

or, in terms of first-order populations and coherences,

$$\begin{aligned}\frac{d\rho_{nn}^{(1)}}{dt}&=-\frac{i}{\hbar}\sum_m (H'_{nm}\rho_{mn}^{(0)}-\rho_{nm}^{(0)}H'_{mn})-\sum_m \Gamma_{n:m}\rho_{mm}^{(1)} ,\\ \frac{d\rho_{nm}^{(1)}}{dt}&=-(i\omega_{nm}+\Gamma_{nm})\rho_{nm}^{(1)}-\frac{i}{\hbar}\sum_l (H'_{nl}\rho_{lm}^{(0)}-\rho_{nl}^{(0)}H'_{lm}) .\end{aligned} \tag{2.11}$$

Using the zeroth-order solutions (2.9), these equations can be simplified to yield

$$\frac{d\rho_{nn}^{(1)}}{dt}=-\sum_m \Gamma_{n:m}\rho_{mm}^{(1)} , \tag{2.12}$$

$$\frac{d\rho_{nm}^{(1)}}{dt}=(i\omega_{nm}+\Gamma_{nm})\rho_{nm}^{(1)}+\frac{i}{\hbar}H'_{nm}(\rho_{nn}^0-\rho_{mm}^0) . \tag{2.13}$$

At the initial time there is no first-order correction $\rho_{nn}^{(1)}(0)=0$, which in turn implies that for (2.12) we have

$$\rho_{nn}^{(1)}(t)=0 . \tag{2.14}$$

Moreover, the formal solution to (2.13) takes the form

$$\rho_{nm}^{(1)}(t)=\frac{i}{\hbar}(\rho_{nn}^0-\rho_{mm}^0)\int_0^t dt_1\, H'_{nm}(t_1)e^{i\omega'_{nm}(t_1-t)} , \tag{2.15}$$

where the notation $\omega'_{nm}=\omega_{nm}-i\Gamma_{nm}$ has been introduced.

We are now concerned with the second-order contributions to population and coherences. The starting relation is

$$\frac{d\rho^{(2)}}{dt}=-iL_0\rho^{(2)}-iL'\rho^{(1)}-\Gamma\rho^{(2)} . \tag{2.16}$$

Consequently, populations and coherences satisfy the equations

$$\frac{d\rho_{nn}^{(2)}}{dt}=-\frac{i}{\hbar}\sum_m (H'_{nm}\rho_{mn}^{(1)}-\rho_{nm}^{(1)}H'_{mn})-\sum_m \Gamma_{n:m}\rho_{mm}^{(2)} \tag{2.17}$$

and

$$\frac{d\rho_{nm}^{(2)}}{dt}=-(i\omega_{nm}+\Gamma_{nm})\rho_{nm}^{(2)}-\frac{i}{\hbar}\sum_{l}(H'_{nl}\rho_{lm}^{(1)}-\rho_{nl}^{(1)}H'_{lm}) , \tag{2.18}$$

respectively. Introducing the first-order corrections previously determined, the contributions to the second-order coherences are now given by

$$\frac{d\rho_{nm}^{(2)}}{dt}=-(i\omega_{nm}+\Gamma_{nm})\rho_{nm}^{(2)}-\frac{i}{\hbar}\sum_{\substack{l\\(n\neq l\neq m)}}(H'_{nl}\rho_{lm}^{(1)}-\rho_{nl}^{(1)}H'_{lm}) . \tag{2.19}$$

This equation clearly states that for a two-level system, the second term on the right-hand side does not exist and hence $\rho_{nm}^{(2)}=0$. That is, there is no second-order term $\rho_{nm}^{(2)}$ for a two-level system. In the more general case of a many level system, Eq. (2.19) can easily be solved

$$\rho_{nm}^{(2)}(t)=-\frac{i}{\hbar}\int_{0}^{t}dt_1\, e^{i\omega'_{nm}(t_1-t)}\times\sum_{l}{}''\,[H'_{nl}(t_1)\rho_{lm}^{(1)}(t_1)-\rho_{nl}^{(1)}(t_1)H'_{lm}(t_1)] , \tag{2.20}$$

where the symbol $\sum_{l}''$ excludes summation over $l=n,m$. Using the expression (2.15) for the coherences, we obtain

$$\rho_{nm}^{(2)}=\frac{i}{\hbar^2}\sum_{l}{}''\int_{0}^{t}dt_1\int_{0}^{t_1}dt_2\, e^{i\omega'_{nm}(t_1-t)}[(\rho_{ll}^{0}-\rho_{mm}^{0})H'_{nl}(t_1)H'_{lm}(t_2)e^{i\omega'_{lm}(t_2-t_1)}+(\rho_{ll}^{0}-\rho_{nn}^{0})H'_{nl}(t_2)H'_{lm}(t_1)e^{i\omega'_{nl}(t_2-t_1)}] . \tag{2.21}$$

We still have to solve Eq. (2.17). In order to show how this can be done in general, we first consider the specific cases of two- and three-level systems. For a two-level system (a,b) we have

$$\frac{d\rho_{aa}^{(2)}}{dt}=-\frac{i}{\hbar}(H'_{ab}\rho_{ba}^{(1)}-\rho_{ab}^{(1)}H'_{ba})-\Gamma_{a:a}\rho_{aa}^{(2)}-\Gamma_{a:b}\rho_{bb}^{(2)} . \tag{2.22}$$

Using the relations

$$\begin{aligned}&\rho_{aa}^{(2)}+\rho_{bb}^{(2)}=0 ,\\&\Gamma_{a:b}=-\Gamma_{b:b} ,\end{aligned} \tag{2.23}$$

the formal solution to Eq. (2.22) is given by

$$\rho_{aa}^{(2)}(t)=-\frac{i}{\hbar}\int_{0}^{t}dt_1 e^{\Gamma_1(t_1-t)}[H'_{ab}(t_1)\rho_{ba}^{(1)}(t_1)-\rho_{ab}^{(1)}(t_1)H'_{ba}(t_1)] , \tag{2.24}$$

where $\Gamma_1=\Gamma_{a:a}+\Gamma_{b:b}$. Substituting Eq. (2.15) into Eq. (2.24), we finally get

$$\rho_{aa}^{(2)}(t)=\frac{1}{\hbar^2}(\rho_{bb}^{0}-\rho_{aa}^{0})\int_{0}^{t}dt_1\int_{0}^{t_1}dt_2\, e^{\Gamma_1(t_1-t)}[H'_{ab}(t_1)H'_{ba}(t_2)e^{i\omega'_{ba}(t_2-t_1)}+H'_{ab}(t_2)H'_{ba}(t_1)e^{i\omega'_{ab}(t_2-t_1)}] . \tag{2.25}$$

Next, we consider the solution for a three-level system that will be of interest in the following. Notice that in this case

$$\rho_{aa}^{(2)}+\rho_{bb}^{(2)}+\rho_{cc}^{(2)}=0 , \tag{2.26}$$

so that

$$\begin{aligned}\frac{d\rho_{bb}^{(2)}}{dt}&=f_b(t)-(\Gamma_{b:b}-\Gamma_{b:a})\rho_{bb}^{(2)}-(\Gamma_{b:c}-\Gamma_{b:a})\rho_{cc}^{(2)} ,\\\frac{d\rho_{cc}^{(2)}}{dt}&=f_c(t)-(\Gamma_{c:c}-\Gamma_{c:a})\rho_{cc}^{(2)}-(\Gamma_{c:b}-\Gamma_{c:a})\rho_{bb}^{(2)} ,\end{aligned} \tag{2.27}$$

where

$$f_p(t)=-\frac{i}{\hbar}\sum_{m\ (\neq p)}(H'_{pm}\rho_{mp}^{(1)}-\rho_{pm}^{(1)}H'_{mp}),\quad p=b,c . \tag{2.28}$$

Equation (2.27) can be solved by using the Laplace transform method. The solutions can be expressed in the form

$$\rho_{bb}^{(2)}(t)=\frac{1}{\lambda_1-\lambda_2}\int_{0}^{t}dt_1\{f_b(t-t_1)[(c_c-\lambda_2)e^{-\lambda_2t_1}+(\lambda_1-c_c)e^{-\lambda_1t_1}]-b_cf_c(t-t_1)(e^{-\lambda_2t_1}-e^{-\lambda_1t_1})\} \tag{2.29}$$

and

$$\rho_{cc}^{(2)}(t)=\frac{1}{\lambda_1-\lambda_2}\int_{0}^{t}dt_1\{f_c(t-t_1)[(b_b-\lambda_2)e^{-\lambda_2t_1}+(\lambda_1-b_b)e^{-\lambda_1t_1}]-c_bf_b(t-t_1)(e^{-\lambda_2t_1}-e^{-\lambda_1t_1})\} , \tag{2.30}$$

where the following notations have been introduced

$$\begin{aligned}
&\lambda_1=\tfrac{1}{2}(b_b+c_c)+\tfrac{1}{2}[(c_c-b_b)^2+4c_b b_c]^{1/2}\ ,\\
&\lambda_2=\tfrac{1}{2}(b_b+c_c)-\tfrac{1}{2}[(c_c-b_b)^2+4c_b b_c]^{1/2}\ ,\\
&b_b=\Gamma_{b:b}-\Gamma_{b:a},\quad b_c=\Gamma_{b:c}-\Gamma_{b:a}\ ,\\
&c_c=\Gamma_{c:c}-\Gamma_{c:a};\quad c_b=\Gamma_{c:b}-\Gamma_{c:a}\ ,
\end{aligned} \tag{2.31}$$

and

$$f_p(t)=\frac{1}{\hbar^2}\sum_{m\,(\neq p)}(\rho^0_{mm}-\rho^0_{pp})\int_0^t dt_1[H'_{pm}(t)H'_{mp}(t_1)e^{i\omega'_{mp}(t_1-t)}+H'_{pm}(t_1)H'_{mp}(t)e^{i\omega'_{pm}(t_1-t)}],\quad p=b,c\ . \tag{2.32}$$

We are now ready to evaluate to the third-order approximation which is the main goal of the present work. The starting equation is

$$\frac{d\rho^{(3)}}{dt}=-iL_0\rho^{(3)}-iL'\rho^{(2)}-\Gamma\rho^{(3)} \tag{2.33}$$

or, in terms of populations and coherences,

$$\frac{d\rho^{(3)}_{nn}}{dt}=-\frac{i}{\hbar}\sum_m(H'_{nm}\rho^{(2)}_{mn}-\rho^{(2)}_{nm}H'_{mn})-\sum_m\Gamma_{n:m}\rho^{(3)}_{mm}\ , \tag{2.34}$$

$$\begin{aligned}\frac{d\rho^{(3)}_{nm}}{dt}&=-(i\omega_{nm}+\Gamma_{nm})\rho^{(3)}_{nm}-\frac{i}{\hbar}H'_{nm}(\rho^{(2)}_{mm}-\rho^{(2)}_{nn})\\
&\quad-\frac{i}{\hbar}\sum_l{}''(H'_{nl}\rho^{(2)}_{lm}-\rho^{(2)}_{nl}H'_{lm})\ .\end{aligned} \tag{2.35}$$

Of course, in treating four-wave mixing experiments, $\rho^{(3)}_{nm}$ is the basic quantity required to evaluate the polarization. Then, depending on the type of geometry used, the corresponding physical observables can be calculated. For instance, if we are interested in phase conjugation spectroscopy, the observable will be the conjugated wave and so on. In any case we always need to evaluate $\rho^{(3)}_{nm}$. From expression (2.35) we get the formal result

$$\rho^{(3)}_{nm}(t)=[\rho^{(3)}_{nm}(t)]_1+[\rho^{(3)}_{nm}(t)]_2\ , \tag{2.36}$$

where

$$\begin{aligned}[\rho^{(3)}_{nm}(t)]_1&=-\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{nm}(t_1-t)}H'_{nm}(t_1)\\
&\quad\times[\rho^{(2)}_{mm}(t_1)-\rho^{(2)}_{nn}(t_1)]\ ,\end{aligned} \tag{2.37}$$

$$\begin{aligned}[\rho^{(3)}_{nm}(t)]_2&=-\frac{i}{\hbar}\sum_l{}''\int_0^t dt_1 e^{i\omega'_{nm}(t_1-t)}\\
&\quad\times[H'_{nl}(t_1)\rho^{(2)}_{lm}(t_1)\\
&\quad-\rho^{(2)}_{nl}(t_1)H'_{lm}(t_1)]\ .\end{aligned} \tag{2.38}$$

It is remarkable that for two-level systems only the first term contributes to the coherences. From an inspection of relation (2.37), it appears that third-order coherences $\rho^{(3)}_{nm}(t)$ are generated only by second-order populations $\rho^{(2)}_{mm}(t)$. It is worth mentioning that because of the extensive use of two-level models in nonlinear optics, only $[\rho^{(3)}_{nm}(t)]_1$ is considered in these descriptions. Therefore it is important to get some insights into the contributions arising from second-order populations and coherences, as well as about their relative importance.

As a first step we shall evaluate the formal expressions of these contributions for two- and three-level systems. For a two- level system, we have

$$\rho^{(3)}_{ab}(t)=[\rho^{(3)}_{ab}(t)]_1+[\rho^{(3)}_{ab}(t)]_2=[\rho^{(3)}_{ab}(t)]_1\ , \tag{2.39}$$

where

$$[\rho^{(3)}_{ab}(t)]_1=\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)[\rho^{(2)}_{aa}(t_1)-\rho^{(2)}_{bb}(t_1)]\ . \tag{2.40}$$

Recalling that $\rho^{(2)}_{aa}+\rho^{(2)}_{bb}=0$ and using Eq. (2.25), we obtain

$$\begin{aligned}\rho^{(3)}_{ab}(t)&=\frac{2i}{\hbar^3}(\rho^0_{bb}-\rho^0_{aa})\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)e^{\Gamma_1(t_2-t_1)}\\
&\quad\times[H'_{ab}(t_2)H'_{ba}(t_3)e^{i\omega'_{ba}(t_3-t_2)}+H'_{ab}(t_3)H'_{ba}(t_2)e^{i\omega'_{ab}(t_3-t_2)}]\ .\end{aligned} \tag{2.41}$$

For a three-level system, the first contribution is

$$[\rho^{(3)}_{ab}(t)]_1=\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)[\rho^{(2)}_{aa}(t_1)-\rho^{(2)}_{bb}(t_1)]\ , \tag{2.42}$$

where, as previously mentioned, the relation $\sum_i\rho^{(2)}_{ii}=0$ can be used. Notice that $\rho^{(2)}_{bb}(t)$ and $\rho^{(2)}_{cc}(t)$ are given by Eqs. (2.29) and (2.30). The extra contribution $[\rho^{(3)}_{ab}(t)]_2$, nonzero for systems with more than two levels only, takes the form

$$[\rho_{ab}^{(3)}(t)]_2 = -\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}[H'_{ac}(t_1)\rho_{cb}^{(2)}(t_1) - \rho_{ac}^{(2)}(t_1)H'_{cb}(t_1)] , \tag{2.43}$$

where

$$\rho_{ac}^{(2)}(t) = \frac{1}{\hbar^2}\int_0^t dt_1\int_0^{t_1} dt_2 e^{i\omega'_{ac}(t_1-t)}[(\rho_{bb}^0-\rho_{cc}^0)H'_{ab}(t_1)H'_{bc}(t_2)e^{i\omega'_{bc}(t_2-t_1)} + (\rho_{bb}^0-\rho_{aa}^0)H'_{ab}(t_2)H'_{bc}(t_1)e^{i\omega'_{ab}(t_2-t_1)}] , \tag{2.44}$$

$$\rho_{cb}^{(2)}(t) = \frac{1}{\hbar^2}\int_0^t dt_1\int_0^{t_1} dt_2 e^{i\omega'_{cb}(t_1-t)}[(\rho_{aa}^0-\rho_{bb}^0)H'_{ca}(t_1)H'_{ab}(t_2)e^{i\omega'_{ab}(t_2-t_1)} + (\rho_{aa}^0-\rho_{cc}^0)H'_{ca}(t_2)H'_{ab}(t_1)e^{i\omega'_{ca}(t_2-t_1)}] . \tag{2.45}$$

From the previous results for two- and three-level systems, we can see that the existence of a third level c not only makes $[\rho_{ab}^{(3)}(t)]_2$ nonzero but also changes $[\rho_{ab}^{(3)}(t)]_1$. These differences and their consequences will be analyzed in more details in Sec. IV of this work. Here, we just note that if we set $H'_{ac}=0$ and $H'_{bc}=0$ in Eqs. (2.41)–(2.45) we obtain $\rho_{ab}^{(3)}$ for the so-called pseudo-two-level systems treated by Duppen and Wiersma.[13]

III. OPTICAL SUSCEPTIBILITIES

The aim of this section is to present a simple derivation of the nonlinear optical susceptibilities $X^{(n)}$ for $n=1$, 2, and 3. As is well known, a material system experiencing optical fields will develop a polarization **P**. In the case where the response of the system can be considered to be instantaneous, **P** is a function of the electric fields in the mathematical sense. Therefore, the macroscopic polarization may be expressed as an expansion of powers of **E**,

$$P_i = X_{ij}^{(1)}E_j + X_{ijk}^{(2)}E_jE_k + X_{ijkl}^{(3)}E_jE_kE_l + \cdots , \tag{3.1}$$

where P_i is the ith component of the polarization and E_j the j component of the electric field acting on the molecule. Also $X^{(n)}$ is an nth-rank tensor and is frequency dependent. Note that for a delayed polarization some care concerning the ordering of the fields must be taken for the third-order susceptibility. The total electric field takes the form

$$\mathbf{E} = \tfrac{1}{2}\sum_\alpha \mathbf{E}_\alpha e^{-i(\omega_\alpha t - \mathbf{k}_\alpha\cdot\mathbf{r})} + \text{c.c.} , \tag{3.2}$$

where the symbol c.c. stands for the complex conjugate part. For convenience, the polarization is also written as

$$\mathbf{P} = \tfrac{1}{2}\sum_\alpha \mathbf{P}_\alpha e^{-i(\omega_\alpha t - \mathbf{k}_\alpha\cdot\mathbf{r})} + \text{c.c.} \tag{3.3}$$

To calculate the first three orders of the nonlinear susceptibility, we shall make use of the quantities $\rho_{nm}^{(1)}$, $\rho_{nm}^{(2)}$, and $\rho_{nm}^{(3)}$ given in Sec. II. Also with the notation introduced for the fields, the radiation-matter interaction can be explicited in the form

$$H'(t) = -\boldsymbol{\mu}\cdot\mathbf{E}(t) = -\tfrac{1}{2}\sum_\alpha \boldsymbol{\mu}\cdot(\mathbf{E}_\alpha e^{-i(\omega_\alpha t - \mathbf{k}_\alpha\cdot\mathbf{r})} + \text{c.c.}) , \tag{3.4}$$

where $\boldsymbol{\mu}$ is the dipole operator.

From relation (2.4), the first-order contribution to the polarization is

$$\mathbf{P}^{(1)} = \text{Tr}(\rho^{(1)}\boldsymbol{\mu}) = \sum_{n,m}\rho_{nm}^{(1)}\boldsymbol{\mu}_{mn} . \tag{3.5}$$

Substituting Eq. (2.15) and carrying out the integration with respect to t_1, we obtain, for times longer than the characteristic times of the medium Γ_{nm}^{-1} or Γ_{nn}^{-1},

$$\mathbf{P}^{(1)} = -\frac{1}{2\hbar}\sum_n\sum_m\sum_\alpha(\rho_{nn}^0-\rho_{mm}^0)\boldsymbol{\mu}_{mn} \times\left[\frac{\boldsymbol{\mu}_{nm}\cdot\mathbf{E}_\alpha}{-\omega_\alpha+\omega'_{nm}}e^{-i(\omega_\alpha t-\mathbf{k}_\alpha\cdot\mathbf{r})} + \frac{\boldsymbol{\mu}_{nm}\cdot\mathbf{E}_\alpha^*}{\omega_\alpha+\omega'_{nm}}e^{i(\omega_\alpha t-\mathbf{k}_\alpha\cdot\mathbf{r})}\right] . \tag{3.6}$$

The first-order susceptibility at frequency ω_α is obtained in the form

$$X_{ij}^{(1)}(\omega_\alpha) = \frac{1}{\hbar}\sum_n\sum_m\sum_\alpha(\rho_{nn}^0-\rho_{mm}^0)\frac{\mu_{mn}^{(i)}\mu_{nm}^{(j)}}{\omega_\alpha-\omega'_{nm}} , \tag{3.7}$$

where $\mu_{mn}^{(i)}$ represents the ith vector component of $\boldsymbol{\mu}_{mn}$. Now, we look at the second-order optical susceptibility. Notice that

$$\mathbf{P}^{(2)} = \sum_m\sum_n\rho_{nm}^{(2)}\boldsymbol{\mu}_{mn} , \tag{3.8}$$

as previously. Therefore, substituting Eq. (2.21) and carrying out the double time integration, we obtain

$$\mathbf{P}^{(2)} = -\frac{1}{4\hbar^2}\sum_\alpha\sum_\beta\sum_m\sum_n\sum_l\frac{\boldsymbol{\mu}_{mn}(\boldsymbol{\mu}_{nl}\cdot\mathbf{E}_\alpha)(\boldsymbol{\mu}_{lm}\cdot\mathbf{E}_\beta)}{\omega'_{nm}-\omega_\alpha-\omega_\beta}e^{-it(\omega_\alpha+\omega_\beta)}e^{i(\mathbf{k}_\alpha+\mathbf{k}_\beta)\cdot\mathbf{r}}\left[\frac{\rho_{ll}^0-\rho_{mm}^0}{\omega'_{lm}-\omega_\beta}+\frac{\rho_{ll}^0-\rho_{nn}^0}{\omega'_{nl}-\omega_\alpha}\right] . \tag{3.9}$$

It should be noted that for two-level systems we have shown that $\rho_{nm}^{(2)}=0$ for $m\neq n$ and hence $X^{(2)}=0$. For larger systems the second-order susceptibilities at frequencies $(\omega_\alpha,\omega_\beta)$ is straightforwardly obtained as

$$X_{ijk}^{(2)}(\omega_\alpha,\omega_\beta)=-\frac{1}{\hbar^2}\sum_\alpha\sum_\beta\sum_m\sum_n\sum_l\frac{\mu_{mn}^{(i)}\rho_{nl}^{(j)}\mu_{lm}^{(k)}}{\omega'_{nm}-\omega_\alpha-\omega_\beta}\times\left[\frac{\rho_{ll}^0-\rho_{mm}^0}{\omega'_{lm}-\omega_\beta}+\frac{\rho_{ll}^0-\rho_{nn}^0}{\omega'_{nl}-\omega_\alpha}\right]. \tag{3.10}$$

Finally, we consider the third-order susceptibility. The basic relation is

$$\mathbf{P}^{(3)}=\sum_m\sum_n\rho_{nm}^{(3)}\boldsymbol{\mu}_{mn}\ . \tag{3.11}$$

From Eq. (2.36) we can see that $\rho_{nm}^{(3)}(t)$ can be separated into two parts so that

$$\mathbf{P}^{(3)}=\mathbf{P}_1^{(3)}+\mathbf{P}_2^{(3)}\ , \tag{3.12}$$

where

$$\mathbf{P}_1^{(3)}=\sum_m\sum_n[\rho_{nm}^{(3)}(t)]_1\boldsymbol{\mu}_{mn}=-\frac{i}{\hbar}\sum_m\sum_n\boldsymbol{\mu}_{mn}\int_0^t dt_1 e^{i\omega'_{nm}(t_1-t)}H'_{nm}(t_1)\times[\rho_{mm}^{(2)}(t_1)-\rho_{nn}^{(2)}(t_1)] \tag{3.13}$$

and

$$P_2^{(3)}=\sum_m\sum_n[\rho_{nm}^{(3)}(t)]_2\boldsymbol{\mu}_{mn}=-\frac{i}{\hbar}\sum_m\sum_n\sum_l{}''\boldsymbol{\mu}_{mn}\int_0^t dt_1 e^{i\omega'_{nm}(t_1-t)}\times[H'_{nl}(t_1)\rho_{lm}^{(2)}(t_1)-\rho_{lm}^{(2)}(t_1)H'_{lm}(t_1)]\ . \tag{3.14}$$

In other words, $\mathbf{P}_1^{(3)}$ is due to the contributions from the diagonal elements $\rho_{nn}^{(2)}$ and $\rho_{mm}^{(2)}$, while $\mathbf{P}_2^{(3)}$ is due to the contributions from the off-diagonal elements $\rho_{lm}^{(2)}$ and $\rho_{nl}^{(2)}$. The conventional expression for $X^{(3)}$ in treating coherent anti-Stokes Raman spectroscopy (CARS) and coherent Stokes-Raman spectroscopy (CSRS) (Ref. 14) is obtained solely from $\mathbf{P}_2^{(3)}$; that is, the contribution from $P_1^{(3)}$ is neglected. On the other hand, for two-level systems, as used, for example, in transient analysis of optical phase conjugation, $\mathbf{P}_2^{(3)}=0$ and $\mathbf{P}_1^{(3)}$ only contributes to $X^{(3)}$.

Here, we just derive the conventional expression $\mathbf{P}_2^{(3)}$ for $X^{(3)}$ and leave for the Appendix its explicit calculation for two- and three-level systems. Substituting Eq. (2.21) into Eq. (3.14) yields

$$\mathbf{P}_2^{(3)}=-\frac{1}{8\hbar^3}\sum_{m,n}\sum_p{}''\sum_{\alpha,\beta,\gamma}\frac{e^{-it(\omega_\alpha+\omega_\beta+\omega_\gamma)}e^{i(\mathbf{k}_\alpha+\mathbf{k}_\beta+\mathbf{k}_\gamma)\cdot\mathbf{r}}}{\omega'_{nm}-\omega_\alpha-\omega_\beta-\omega_\gamma}\times\left[\sum_{\substack{q\\(p\neq q\neq m)}}\frac{\boldsymbol{\mu}_{mn}(\boldsymbol{\mu}_{pq}\cdot\mathbf{E}_\alpha)(\boldsymbol{\mu}_{qm}\cdot\mathbf{E}_\beta)(\boldsymbol{\mu}_{np}\cdot\mathbf{E}_\gamma)}{\omega'_{pm}-\omega_\alpha-\omega_\beta}\left[\frac{\rho_{qq}^0-\rho_{mm}^0}{\omega'_{qm}-\omega_\beta}+\frac{\rho_{qq}^0-\rho_{pp}^0}{\omega'_{pq}-\omega_\alpha}\right]+\sum_{\substack{q\\(p\neq q\neq n)}}\frac{\boldsymbol{\mu}_{mn}(\boldsymbol{\mu}_{nq}\cdot\mathbf{E}_\alpha)(\boldsymbol{\mu}_{qp}\cdot\mathbf{E}_\beta)(\boldsymbol{\mu}_{pm}\cdot\mathbf{E}_\gamma)}{\omega'_{np}-\omega_\alpha-\omega_\beta}\left[\frac{\rho_{pp}^0-\rho_{qq}^0}{\omega'_{qp}-\omega_\beta}+\frac{\rho_{nn}^0-\rho_{qq}^0}{\omega'_{nq}-\omega_\alpha}\right]\right]. \tag{3.15}$$

From the ith component of the polarization and the j, k, and l components of the fields $\mathbf{E}_\alpha$, $\mathbf{E}_\beta$, and $\mathbf{E}_\gamma$, respectively, we obtain the following expression for the third-order nonlinear susceptibility:

$$X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)=-\frac{1}{\hbar^3}\sum_{nm}\sum_p{}''\sum_{\alpha\beta\gamma}\frac{1}{\omega'_{nm}-\omega_\alpha-\omega_\beta-\omega_\gamma}\times\left[\sum_{\substack{q\\(p\neq q\neq m)}}\frac{\mu_{mn}^{(i)}\mu_{pq}^{(j)}\mu_{qm}^{(k)}\mu_{np}^{(l)}}{\omega'_{pm}-\omega_\alpha-\omega_\beta}\left[\frac{\rho_{qq}^0-\rho_{mm}^0}{\omega'_{qm}-\omega_\beta}+\frac{\rho_{qq}^0-\rho_{pp}^0}{\omega'_{pq}-\omega_\alpha}\right]+\sum_{\substack{q\\(p\neq q\neq n)}}\frac{\mu_{mn}^{(i)}\mu_{nq}^{(j)}\mu_{qp}^{(i)}\mu_{pm}^{(l)}}{\omega'_{np}-\omega_\alpha-\omega_\beta}\left[\frac{\rho_{pp}^0-\rho_{qq}^0}{\omega'_{qp}-\omega_\beta}+\frac{\rho_{nn}^0-\rho_{qq}^0}{\omega'_{nq}-\omega_\alpha}\right]\right]. \tag{3.16}$$

These expressions for $X^{(2)}$ and $X^{(3)}$ are quite general and can be applied to various nonlinear optical processes.

IV. COHERENCE-POPULATION INTERDEPENDENCE IN PRESENCE OF A PERTURBATING LEVEL

The present section is devoted to the analysis of relations existing between coherences and populations. We have shown previously that when a system has more than two levels, an additional contribution to the third-order coherence appears generated by second-order coherence. In order to stress the importance of this contribution,[15] we introduce a model system with the following characteristics. The nonlinear medium has a ground state a, an excited state b radiatively coupled to the ground state by dipolar interaction, and a second excited state c with no dipolar interaction and playing the role of a perturbation. Both excited levels interact weakly. This model is frequently encountered in the description of nonradiative processes of organic systems except that we usually have a distribution of perturbating levels. Sometimes the density of the perturbating states and their corresponding couplings are such that the manifold of states acts like a dissipative quasicontinuum. Then, the Bloch-equation treatment of Friedmann *et al.*[16] in which the interactions are treated in a purely phenomenological fashion is well adapted. The couplings between the excited state $|b\rangle$ and the manifold, a set of states $|c\rangle$, are accounted for by a nonradiative transition rate constant. Such a case corresponds typically to the statistical limit case of large molecules like, for instance, on intersystem crossing in benzene[17] or on the $S_2 \rightarrow S_1$ internal conversion in any large molecule.[18] In some other molecules, because of symmetry selection rules, only few levels of the degenerate quasicontinuum are significantly coupled to the excited state. For the sake of simplicity, we limit our model to the case of sparsely distributed perturbating levels, so that only one of them acts efficiently. This situation could characterize the intermediate molecule or small molecule limit cases. For instance, our model is typically required to explain the Douglas effect responsible of the longest-lived excited states in small molecules.[19] It could be of interest to have an estimate of $|V_{bc}|$ for real systems. Perhaps the best evaluation of $|V_{bc}|$ can be deduced from systems where this coupling is able to generate quantum beats in the fluorescence. There is a number of examples in the literature. Typical observations on molecular systems are quantum beats in the fluorescence decay of jet-cooled anthracene excited by picosecond pulses,[20,21] or those obtained in biacethyl and methylglyoxal as resulting from singlet-triplet coupling.[22] An interesting evaluation of the coupling $|V_{bc}|$ has been done by Henke *et al.*[23] from their experimental results on collision and magnetic field effects on quantum beats in biacethyl. They obtained an estimate of the order of 1.15 MHz for $|V_{bc}|$, say, H_{mn} in their work. A different approach could be developed to introduce the coupling V_{bc}. It would imply the description of the internal dynamics of the molecule in the V-prediagonalized basis set. However, a proper account of the decay and dephasing processes then requires a redefinition of the various matrix elements of the damping operator. The energy diagram is given in Fig. 1. Therefore, the matrix representation in terms of states a, b, and c corresponds to

$$H^0 = \begin{vmatrix} \hbar\omega_a & 0 & 0 \\ 0 & \hbar\omega_b & V_{bc} \\ 0 & V_{cb} & \hbar\omega_c \end{vmatrix} . \tag{4.1}$$

Also, the only nonzero matrix elements of the damping operator are $\Gamma_{b:b} = -\Gamma_{a:b}$.

In order to estimate the influence of a third level it is better to treat the interaction V exactly and not as a perturbation. Therefore, the basic equation for the kth-order perturbation in the field-matter interaction is

$$\frac{d}{dt}\rho^{(k)} = -\frac{i}{\hbar}[H^0,\rho^{(k)}] - \frac{i}{\hbar}[H'(t),\rho^{(k-1)}] - \Gamma\rho^{(k)} . \tag{4.2}$$

In terms of matrix elements, we obtain

$$\begin{aligned} \frac{d}{dt}\rho^{(k)}_{nn} = & -\frac{i}{\hbar}\sum_{l}(H^0_{nl}\rho^{(k)}_{\text{ln}} - \rho^{(k)}_{nl}H^0_{\text{ln}}) \\ & - \sum_{l}\Gamma_{n:l}\rho^{(k)}_{ll} + C^{(k-1)}_{nn} \end{aligned} \tag{4.3}$$

and

$$\begin{aligned} \frac{d}{dt}\rho^{(k)}_{nm} = & \, i\omega'_{nm}\rho^{(k)}_{nm} + \frac{i}{\hbar}H^0_{nm}(\rho^{(k)}_{nn} - \rho^{(k)}_{mm}) \\ & - \frac{i}{\hbar}\sum_{\substack{l \\ (m \neq l \neq n)}}(H^0_{nl}\rho^{(k)}_{lm} - \rho^{(k)}_{nl}H^0_{lm}) \\ & + P^{(k-1)}_{nm} + C^{(k-1)}_{nm} \quad \text{if } n \neq m . \end{aligned} \tag{4.4}$$

The simplifying notations

$$P^{(k-1)}_{\alpha\beta}(t) = \frac{i}{\hbar}H'_{\alpha\beta}(t)[\rho^{(k-1)}_{\alpha\alpha} - \rho^{(k-1)}_{\beta\beta}]$$

and

$$\begin{aligned} C^{(k-1)}_{\alpha\beta}(t) = & -\frac{i}{\hbar}\sum_{l\,(\neq\beta)}H'_{\alpha l}(t)\rho^{(k-1)}_{l\beta} \\ & + \frac{i}{\hbar}\sum_{l\,(\neq\alpha)}\rho^{(k-1)}_{\alpha l}H'_{l\beta}(t) \end{aligned} \tag{4.5}$$

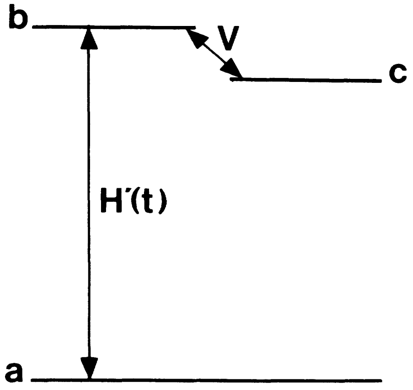

FIG. 1. Energy diagram of the three-level system.

have been introduced. To solve Eqs. (4.3) and (4.4) the Laplace transform is required. With the initial conditions $\rho^{(k)}(0)=0$, we get for $k\neq 0$

$$p\rho_{nn}^{(k)}(p)=-\frac{i}{\hbar}\sum_{l}[H_{nl}^{0}\rho_{\mathrm{ln}}^{(k)}(p)-\rho_{nl}^{(k)}(p)H_{\mathrm{ln}}^{0}] -\sum_{l}\Gamma_{n:l}\,\rho_{ll}^{(k)}(p)+C_{nn}^{(k-1)}(p)\ , \tag{4.6}$$

$$(p+i\omega'_{nm})\rho_{nm}^{(k)}(p)=\frac{i}{\hbar}H_{nm}^{0}[\rho_{nn}^{(k)}(p)-\rho_{mm}^{(k)}(p)] -\frac{i}{\hbar}\sum_{\substack{l\\(m\neq l\neq n)}}[H_{nl}^{0}\rho_{lm}^{(k)}(p)-\rho_{nl}^{(k)}(p)H_{lm}^{0}] +P_{nm}^{(k-1)}(p)+C_{nm}^{(k-1)}(p)\ . \tag{4.7}$$

For convenience, when ρ represents the Laplace transform the p dependence is always explicitly written.

We are now ready to evaluate $\rho_{ab}^{(3)}(p)$. This is done straightforwardly, so we just present here the main lines of the calculation. From Eqs. (4.6) and (4.7) the set of equations for the various coherences and populations of the three-level system is obtained. We get

$$\rho_{ab}^{(3)}(p)=[\rho_{ab}^{(3)}(p)]_1+[\rho_{ab}^{(3)}(p)]_2\ , \tag{4.8}$$

where

$$[\rho_{ab}^{(3)}(p)]_1=f_1(p)P_{ab}^{(2)}(p)\ ,$$
$$[\rho_{ab}^{(3)}(p)]_2=f_2(p)C_{ac}^{(2)}(p)\ . \tag{4.9}$$

$P_{ab}^{(2)}(p)$ and $C_{ac}^{(2)}(p)$ are the Laplace transforms of $P_{ab}^{(2)}(t)$ and $C_{ac}^{(2)}(t)$, respectively. The following notations have been introduced:

$$f_1(p)=[p+i\omega'_{ac}]\Delta(p)\ ,$$
$$f_2(p)=\frac{1}{\hbar}V_{cb}\Delta(p)\ , \tag{4.10}$$
$$\Delta(p)=\left[(p+i\omega'_{ab})(p+i\omega'_{ac})+\frac{1}{\hbar^2}\,|V_{bc}|^2\right]\ .$$

We still have to evaluate $[\rho_{ab}^{(3)}(p)]_i$ for $i=1,2$. In fact, any combination $(\omega_\alpha\pm\omega_\beta\pm\omega_\gamma)$ gives a component to $\rho_{ab}^{(3)}$. We just calculate the component $(\omega_\alpha+\omega_\beta+\omega_\gamma)$, any other one being easily deduced. We begin with the quantity $[\rho_{ab}^{(3)}(p)]_1$. Because we are looking for one particular component, we just need one part of the interaction $H'(t)$, say

$$\Omega_{ab}^{\alpha}e^{-i\omega_\alpha t}=-\tfrac{1}{2}\mu_{ab}E_\alpha e^{-i(\omega_\alpha t-\mathbf{k}_\alpha\cdot\mathbf{r})}\ . \tag{4.11}$$

Therefore the contribution arising from populations is given by

$$[\rho_{ab}^{(3)}(p)]_1=\frac{i}{\hbar}f_1(p)\Omega_{ab}^{\alpha}[\rho_{aa}^{(2)}(p+i\omega_\alpha)-\rho_{bb}^{(2)}(p+i\omega_\alpha)]\ . \tag{4.12}$$

After some algebra, the results can be written in the form

$$[\rho_{ab}^{(3)}(p)]_1=G_1(p)\frac{1}{p+i(\omega_\alpha+\omega_\beta+\omega_\gamma)}\ , \tag{4.13}$$

where $G_1(p)$ is a function with no pole at $p=-i(\omega_\alpha+\omega_\beta+\omega_\gamma)$. A similar structure is obtained for the second contribution generated by the coherences, i.e.,

$$[\rho_{ab}^{(3)}(p)]_2=G_2(p)\frac{1}{p+i(\omega_\alpha+\omega_\beta+\omega_\gamma)}\ . \tag{4.14}$$

The inverse Laplace transforms of these quantities are expressed by

$$[\rho_{ab}^{(3)}(t)]_i=\int_0^t g_i(t_1)e^{-i(\omega_\alpha+\omega_\beta+\omega_\gamma)(t-t_1)}dt_1,\quad i=1,2$$
$$=e^{-i(\omega_\alpha+\omega_\beta+\omega_\gamma)t}\int_0^t g_i(t_1)e^{it_1(\omega_\alpha+\omega_\beta+\omega_\gamma)}\ . \tag{4.15}$$

Notice that if we look for the steady-state solutions, t is longer than any characteristic time of the material system included in $g_i(t)$, the inverse Laplace Transform of $G_i(p)$. Consequently, the time of integration can be extended up to the infinity and we get

$$[\rho_{ab}^{(3)}(t)]_i=e^{-i(\omega_\alpha+\omega_\beta+\omega_\gamma)t}G_i(-i\omega_\alpha-i\omega_\beta-i\omega_\gamma)\ , \tag{4.16}$$

where the expressions of G_i are given by

$$\begin{aligned}
&G_1(-i\omega_\alpha-i\omega_\beta-i\omega_\gamma)\\
&\quad=-\frac{1}{\hbar^5}\Omega_{ab}^{\alpha}\Omega_{ab}^{\beta}\Omega_{ba}^{\gamma}\,|V_{bc}|^2\frac{(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ac})(\omega_\beta+\omega_\gamma-i\Gamma_{b:b})(\omega_\beta+\omega_\gamma-\omega'_{bc})}{E\cdot D\cdot H}\\
&\quad\quad-\frac{1}{\hbar^5}\Omega_{ab}^{\alpha}\Omega_{ba}^{\beta}\Omega_{ab}^{\gamma}\,|V_{bc}|^2\frac{(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ac})(\omega_\beta+\omega_\gamma-i\Gamma_{b:b})(\omega_\beta+\omega_\gamma-\omega'_{cb})}{E\cdot D\cdot F}\\
&\quad\quad-\frac{1}{\hbar^3}\Omega_{ab}^{\alpha}\Omega_{ba}^{\beta}\Omega_{ab}^{\gamma}\left[(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ac})\left[2(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-\omega'_{bc})\right.\right.\\
&\quad\quad\quad\left.\left.-\frac{3}{\hbar^2}\,|V_{bc}|^2[2(\omega_\beta+\omega_\gamma)-(\omega'_{cb}+\omega'_{bc})]\right](\omega_\gamma-\omega'_{ac})\right]\Big/E\cdot D\cdot F\\
&\quad\quad-\frac{1}{\hbar^3}\Omega_{ab}^{\alpha}\Omega_{ab}^{\beta}\Omega_{ba}^{\gamma}\\
&\quad\quad\times\left[(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ac})\left[2(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-\omega'_{cb})(\omega_\beta+\omega_\gamma-\omega'_{bc})\right.\right.\\
&\quad\quad\quad\left.\left.-\frac{3}{\hbar^2}\,|V_{bc}|^2[2(\omega_\beta+\omega_\gamma)-(\omega'_{cb}+\omega'_{bc})]\right](\omega_\gamma-\omega'_{ca})\right]\Big/E\cdot D\cdot H\ ,
\end{aligned} \tag{4.17}$$

$$
\begin{aligned}
G_2(&-i\omega_\alpha-i\omega_\beta-i\omega_\gamma)\\
&=-\frac{1}{\hbar^3}\Omega^\alpha_{ab}\Omega^\beta_{ab}\Omega^\gamma_{ba}\frac{|V_{bc}|^4}{\hbar^4}\frac{2(\omega_\beta+\omega_\gamma)-i\Gamma_{b:b}}{E\cdot D\cdot H}\\
&\quad-\frac{1}{\hbar^3}\Omega^\alpha_{ab}\Omega^\beta_{ba}\Omega^\gamma_{ab}\frac{|V_{bc}|^2}{\hbar^2}\left[\frac{(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-i\Gamma_{b:b})(\omega_\beta+\omega_\gamma-\omega'_{cb})-|V_{bc}|^2[2(\omega_\beta+\omega_\gamma)-i\Gamma_{b:b}]/\hbar^2}{E\cdot D\cdot F}\right]\\
&\quad-\frac{1}{\hbar^3}\Omega^\alpha_{ab}\Omega^\beta_{ba}\Omega^\gamma_{ab}\frac{|V_{bc}|^2}{\hbar^2}\frac{(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-\omega'_{cb})(\omega_\gamma-\omega'_{ac})}{E\cdot D\cdot F}\\
&\quad-\frac{1}{\hbar^3}\Omega^\alpha_{ab}\Omega^\beta_{ab}\Omega^\gamma_{ba}\frac{|V_{bc}|^2}{\hbar^2}\frac{(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-\omega'_{cb})(\omega_\gamma-\omega'_{ca})}{E\cdot D\cdot H}\,,
\end{aligned}
\tag{4.18}
$$

with the following notations:

$$
\begin{aligned}
E&=\left[(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ab})(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ac})-\frac{|V_{bc}|^2}{\hbar^2}\right],\\
D&=(\omega_\beta+\omega_\gamma)(\omega_\beta+\omega_\gamma-i\Gamma_{b:b})(\omega_\beta+\omega_\gamma-\omega'_{cb})(\omega_\beta+\omega_\gamma-\omega'_{bc})-\frac{|V_{bc}|^2}{\hbar^2}[2(\omega_\beta+\omega_\gamma)-(\omega'_{cb}+\omega'_{bc})][2(\omega_\beta+\omega_\gamma)-i\Gamma_{b:b}]\,,\\
F&=\left[(\omega_\gamma-\omega'_{ab})(\omega_\gamma-\omega'_{ac})-\frac{|V_{bc}|^2}{\hbar^2}\right],\quad H=\left[(\omega_\gamma-\omega'_{ba})(\omega_\gamma-\omega'_{ca})-\frac{|V_{bc}|^2}{\hbar^2}\right].
\end{aligned}
\tag{4.19}
$$

We are now ready to analyze the influence of the third perturbating level. This quantitative estimate will be done for the particular case of phase conjugation spectroscopy.

V. APPLICATION TO PHASE CONJUGATION

It is of interest to notice that because of the perturbational approach taken $\rho^{(3)}_{ab}(t)$ has the same frequency components that $H'_{ab}(t)H'_{ab}(t)H'_{ab}(t)$. Therefore by introducing the full interaction terms we have

$$
\begin{aligned}
\rho^{(3)}_{ab}(t)=\sum_j\sum_{\alpha,\beta,\gamma}&[\rho^{(3)}_{ab}(\Omega_j;\omega_\alpha,\omega_\beta,\omega_\gamma)e^{-i\Omega_jt}\\
&+\rho^{(3)}_{ab}(-\Omega_j;\omega_\alpha,\omega_\beta,\omega_\gamma)e^{i\Omega_jt}]\,,
\end{aligned}
\tag{5.1}
$$

where Ω_j stands for one particular combination of $\omega_\alpha\pm\omega_\beta\pm\omega_\gamma$ and where

$$
\rho^{(3)}_{ab}(\Omega_j;\omega_\alpha,\omega_\beta,\omega_\gamma)=\sum_i G_i(-i\omega_\alpha\mp i\omega_\beta\mp i\omega_\gamma)
\tag{5.2}
$$

are the quantities evaluated in Sec. IV. This notation emphasizes the ordering of the interacting fields α, β, and γ.

In the particular case of the phase conjugation spectroscopy the only contribution to the nonlinear polarization are the combinations $\Omega_1=\omega_\alpha+\omega_\beta-\omega_\gamma$ and $\Omega_2=\omega_\alpha-\omega_\beta+\omega_\gamma$. Therefore the spatial components are $\mathbf{k}_\alpha+\mathbf{k}_\beta-\mathbf{k}_\gamma$ with the combinations $(\alpha,\beta,\gamma)=[(1,2,3),(2,1,3)]$ and $\mathbf{k}_\alpha-\mathbf{k}_\beta+\mathbf{k}_\gamma$ with $(\alpha,\beta,\gamma)=[(1,3,2),(2,3,1)]$. For our purpose it suffices to consider the degenerate case, i.e.,

$$
\begin{aligned}
\rho^{(3)}_{ab}(t)=e^{-i\omega t}[\lim_{\omega_1,\omega_2,\omega_3\to\omega}&\{\rho^{(3)}_{ab}(\Omega;\omega_1,\omega_2-\omega_3)+\rho^{(3)}_{ab}(\Omega;\omega_2,\omega_1,-\omega_3)+\rho^{(3)}_{ab}(\Omega;\omega_1,-\omega_3,\omega_2)\\
&+\rho^{(3)}_{ab}(\Omega;\omega_2,-\omega_3,\omega_1)\}]+e^{i\omega t}[\Omega\to-\Omega]\,.
\end{aligned}
\tag{5.3}
$$

In order to compare the contributions resulting from populations and coherences, we have performed numerical calculations on the time-independent factor of $\rho^{(3)}_{ab}(t)$, i.e.,

$$
\Sigma_{ab}(V)=\lim_{\omega_1,\omega_2,\omega_3\to\omega}\{\rho^{(3)}_{ab}(\Omega;\omega_1,\omega_2,-\omega_3)+\rho^{(3)}_{ab}(\Omega;\omega_2,\omega_1,-\omega_3)+\rho^{(3)}_{ab}(\Omega;\omega_1,-\omega_3,\omega_2)+\rho^{(3)}_{ab}(\Omega;\omega_1,-\omega_3,\omega_1)\}\,.
\tag{5.4}
$$

At this stage, it seems necessary to point out some particular features of this calculation. First of all, the comparison between the different terms is best done by comparing the third-order coherences of a two-level system, say $V=0$, to the corresponding quantities for the three-level system in which the coupling V opens a new channel which contributes to $\rho^{(3)}_{ab}(t)$. At this end we will consider the ratio of the real or imaginary part of $\Sigma_{ab}(V)$ with the same quantity in absence of internal interaction, i.e., $\Sigma_{ab}(V=0)$. Next, this ratio is evaluated as a function of the coupling V.

We come now to the second point that we wish to stress here. Usually a comparison of physical quantities must be done by keeping all the physical parameters identical except the one under analysis. The point here is that when the coupling V varies the eigenenergies of the coupled levels b and c shift. Therefore if the same field frequencies are taken in both situations, we are dealing with a two-level system excited on resonance and a three-level system excited off resonance. These situations are no longer comparable because of the supplementary decrease of $\rho_{ab}^{(3)}(t)$ in going from resonance to off resonance. Since the value of the transition frequency is unimportant, for each value of $|V_{bc}|$, we can adjust the frequency of the fields to keep the three-level system resonantly excited like the two-level system we want to compare it to.

We are now ready to start the discussion of the numerical calculation. To emphasize the importance of the coherence-coherence coupling, we compare the quantity $\Sigma_{ab}(V)$ specific to the three-level system to $\Sigma_{ab}(V=0)$ for the corresponding two-level system. At this end we introduce the function

$$R_1=\frac{\mathrm{Re}[\Sigma_{ab}^1(V)]}{\mathrm{Re}[\Sigma_{ab}^1(V=0)]}\ , \tag{5.5}$$

where $\Sigma_{ab}^1(V)$ accounts for the contributions due to populations only. The dependence of R_1 on the coupling strength $|V_{bc}|$ is shown in Fig. 2. It exhibits a rapid increase of R_1, reaches a maximum, and then decreases. From our analytical calculation, we have shown that $|V_{bc}|$ induces a supplementary contribution to $[\rho_{ab}^{(3)}(t)_1]$ responsible for the increase of R_1. Now, as $|V_{bc}|$ becomes more important we observe a redistribution of the dipolar moment over the states b and c which tends to diminish $\Sigma_{ab}^1(V)$ because we keep for all the range of values of $|V_{bc}|$ a resonant excitation of the eigenstate deduced from the state b. Also we have analyzed the influence of the pure dephasing constant. For increasing values of $\Gamma_{bc}^{(d)}$ we note an increase of R_1. In fact, $\rho_{ab}^{(3)}(t)$ is a function of the population

$$|\rho_{aa}^{(2)}(t)-\rho_{bb}^{(2)}(t)|=2\rho_{bb}^{(2)}(t)+\rho_{cc}^{(2)}(t)\ ;$$

as $\Gamma_{bc}^{(d)}$ increases, the population of states b and c increases too and this gives in turn an increase of $\Sigma_{ab}^1(V)$. This observation is in accordance with the result of Friedmann *et al.*[16] In order to have a complete estimate of the population contribution we still have to consider the quantity:

$$I_1=\frac{\mathrm{Im}[\Sigma_{ab}^1(V)]}{\mathrm{Im}[\Sigma_{ab}^1(V=0)]}\ . \tag{5.6}$$

In fact, the ratio of the imaginary parts presents the same dependence previously observed in the R_1 and the same physical explanation holds. See Fig. 3.

Next, we discuss the second type of contribution, that is to say, contributions from the coherences. As above, it can be characterized by the quantities

$$R_2=\frac{\mathrm{Re}[\Sigma_{ab}^2(V)]}{\mathrm{Re}[\Sigma_{ab}^1(V=0)]} \tag{5.7}$$

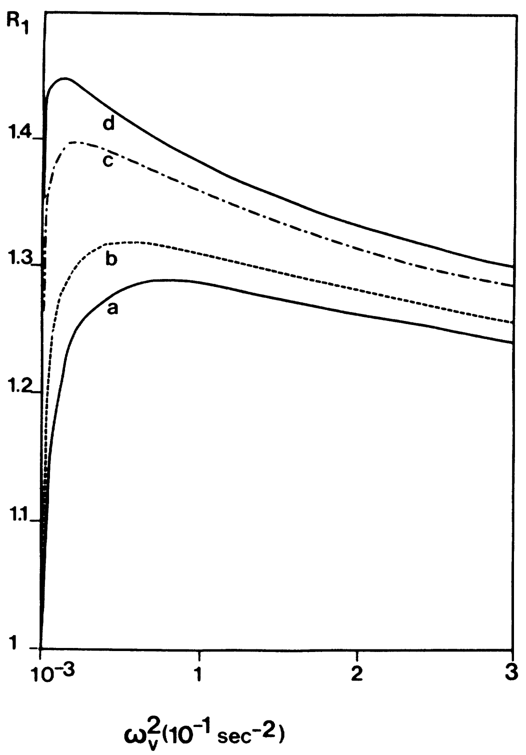

FIG. 2. R_1, the ratio of the real parts of the contributions to the third-order coherence from second-order populations for our three-level system and the corresponding two-level system as a function of ω_v^2 defined by $\omega_v^2=|V_{bc}|^2/\hbar^2$. Various pure dephasing constants are considered [$\Gamma_{bc}^{(d)}=0$ (a), 10^{-4} (b), 5×10^{-4} (c), 10^{-3} (d)]. The values of the other parameters are $E_{ba}=1$, $E_{bc}=0.1$, $\Gamma_{b:b}=10^{-3}$, and $\Gamma_{ab}^{(d)}=10^{-7}$.

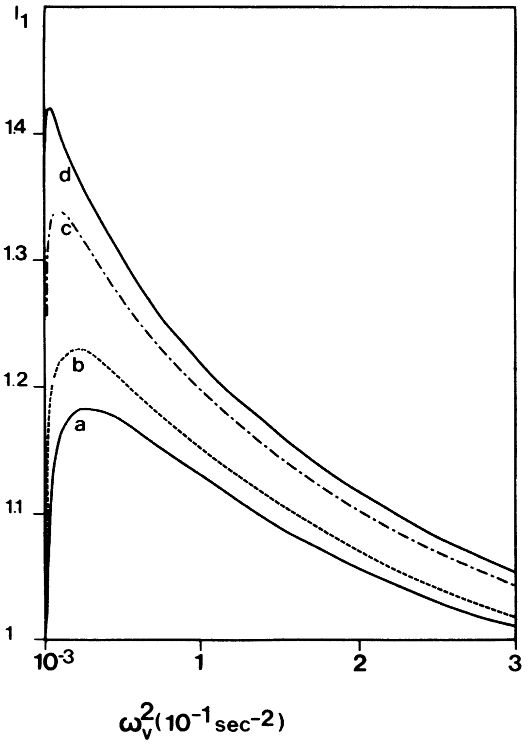

FIG. 3. Same as Fig. 2, but for the ratio of the imaginary parts I_1.

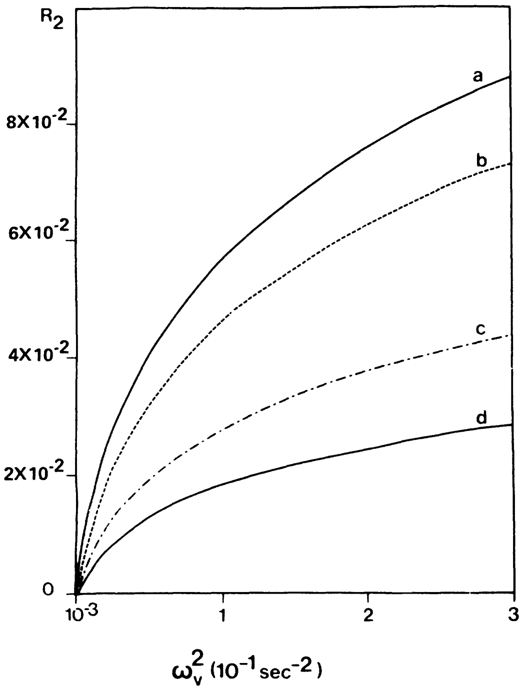

FIG. 4. R_2, the ratio of the real parts of the contributions to the third-order coherence from second-order coherences for the three-level system and from second-order populations for the corresponding two-level system. All else as specified in Fig. 2.

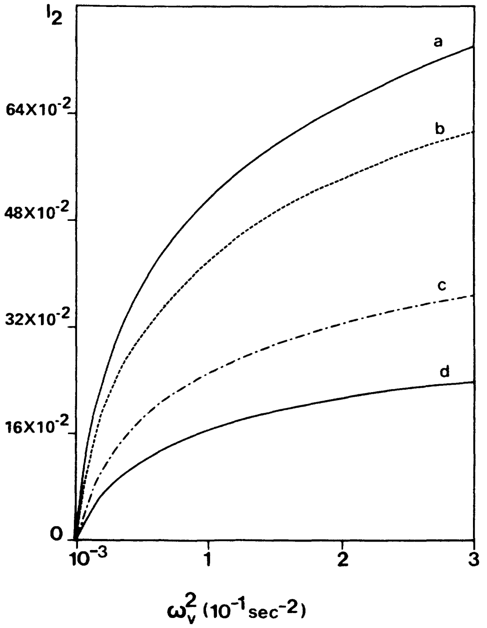

FIG. 5. Same as Fig. 4, but for the ratio of the imaginary parts I_2.

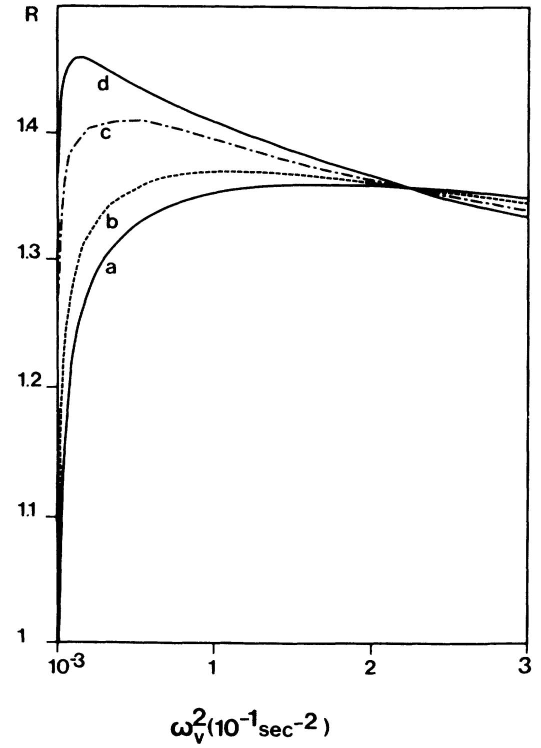

FIG. 6. Plot of R_1+R_2 as resulting from Figs. 2 and 4.

and

$$I_2=\frac{\mathrm{Im}[\Sigma_{ab}^{2}(V)]}{IM[\Sigma_{ab}^{1}(V=0)]}\ , \tag{5.8}$$

which correspond to Figs. 4 and 5, respectively. The symbol $\Sigma_{ab}^2(V)$ stands for the coherence contribution only. Two points must be stressed here. First, we ob-

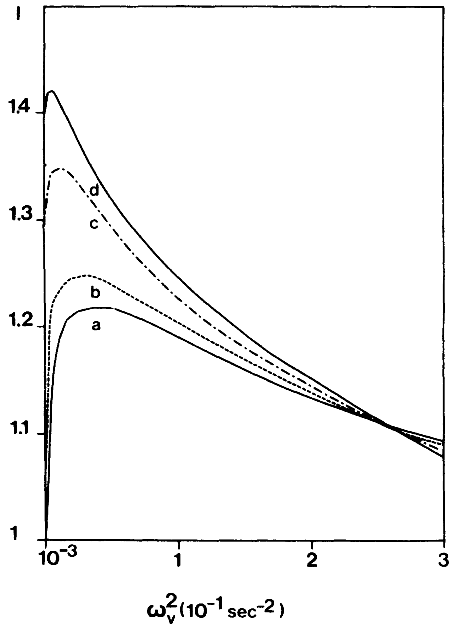

FIG. 7. Plot of I_1+I_2 as resulting from Figs. 3 and 5.

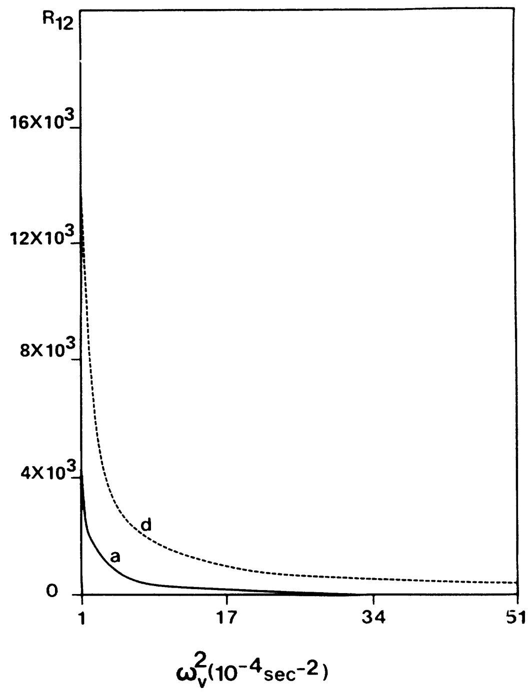

FIG. 8. Plot of R_1/R_2 as resulting from Figs. 2 and 4.

serve a continuous increase of R_2 and I_2 with the increase of the coupling strength $|V_{bc}|$. Second, the pure dephasing constant $\Gamma_{bc}^{(d)}$ has an opposite effect compared to the one described for the population contribution. Here, we notice a decrease of R_2 and I_2 with the increase of $\Gamma_{bc}^{(d)}$. This result is easily understood because for increasing values of $\Gamma_{bc}^{(d)}$ the coherence created by the fields in the system is damped. Figures 6 and 7 represent the sum of the variations previously discussed, i.e.,

$$R=R_1+R_2,\quad I=I_1+I_2\ . \tag{5.9}$$

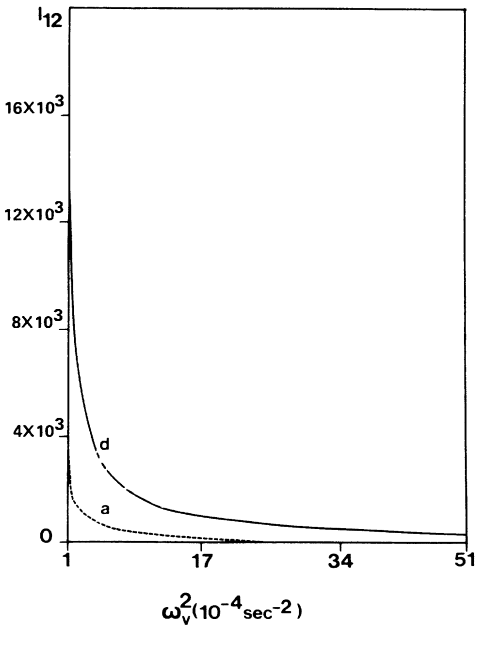

FIG. 9. Plot of I_1/I_2 as resulting from Figs. 3 and 5.

It is interesting to note the existence of fixed point, although for the moment we are unable to give it a precise meaning. Finally to get a better insight into these contributions we still require the knowledge of the ratio $R_{12}=R_1/R_2$ and $I_{12}=I_1/I_2$. Their dependence with $|V_{bc}|$ for various pure dephasing has been depicted on Figs. 8 and 9. From the values shown by these curves there is no doubt that population effects are the predominant ones in the phase conjugation process and that the populations are very sensitive to the presence of perturbating levels.

VI. CONCLUSION

The main goal of this work has been to develop a perturbative many-level system description of four-wave-mixing experiments. At the present stage, only the polarization has been evaluated and any complete description still requires the introduction of this nonlinear polarization into Maxwell equations. Despite the great importance of two-level systems in the description of nonlinear optical processes, it is worth mentioning the sensitivity of the dynamics to the presence of neighboring levels even weakly coupled. Such a situation is frequently encountered in organic materials. We have shown that a perturbating level not only alters the nonlinear polarization generated by populations but also gives an additional contribution resulting from the coherence-coherence coupling. A quantitative estimate of these supplementary contributions has been given. In the future more complex systems will be studied where summation over manifolds of states will be required. We expect that extra contributions to the nonlinear polarization will be even more important in these situations.

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APPENDIX

For comparison we shall calculate $X^{(3)}$ for two- and three-level systems in this appendix. If we consider a two-level system, the basic expression is

$$\mathbf{P}^{(3)}=\rho_{ab}^{(3)}(t)\mu_{ba}+\rho_{ba}^{(3)}(t)\mu_{ab}\ , \tag{A1}$$

where third-order coherence $\rho_{ab}^{(3)}(t)$ has been explicitly calculated previously and is given by Eq. (2.41). Using expressions (3.2) and (3.4) for fields and interaction, respectively, we obtain

$$\rho_{ab}^{(3)}(t)=-\frac{i}{8\hbar^3}(\rho_{bb}^0-\rho_{aa}^0)\sum_{\alpha,\beta,\gamma}\frac{e^{-i(\omega_\alpha+\omega_\beta+\omega_\gamma)t}e^{i(\mathbf{k}_\alpha+\mathbf{k}_\beta+\mathbf{k}_\gamma)\cdot\mathbf{r}}}{(\omega'_{ab}-\omega_\alpha-\omega_\beta-\omega_\gamma)(\omega_\alpha+\omega_\beta+i\Gamma_1)} \times\left[\frac{1}{\omega'_{ab}-\omega_\alpha}+\frac{1}{\omega'_{ba}-\omega_\beta}\right](\boldsymbol{\mu}_{ab}\cdot\mathbf{E}_\gamma)(\boldsymbol{\mu}_{ab}\cdot\mathbf{E}_\alpha)(\boldsymbol{\mu}_{ba}\cdot\mathbf{E}_\beta)\;, \tag{A2}$$

which in turn gives for the nonlinear susceptibility

$$X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)=\frac{i}{4\hbar^3}\sum_{\alpha,\beta,\gamma}\frac{\rho_{aa}^0-\rho_{bb}^0}{\omega_\alpha+\omega_\beta+i\Gamma_1}\left[\frac{1}{\omega'_{ab}-\omega_\alpha}+\frac{1}{\omega'_{ba}-\omega_\beta}\right]\left[\frac{\mu_{ba}^{(i)}\mu_{ab}^{(j)}\mu_{ab}^{(k)}\mu_{ba}^{(l)}}{\omega'_{ab}-\omega_\alpha-\omega_\beta-\omega_\gamma}-\frac{\mu_{ab}^{(i)}\mu_{ba}^{(j)}\mu_{ba}^{(k)}\mu_{ab}^{(l)}}{\omega'_{ba}-\omega_\alpha-\omega_\beta-\omega_\gamma}\right]. \tag{A3}$$

Next we consider three-level systems. As has been pointed out in Sec. II, $\mathbf{P}^{(3)}$ can be written as

$$\mathbf{P}^{(3)}=\mathbf{P}_1^{(3)}+\mathbf{P}_2^{(3)}\;. \tag{A4}$$

Since $\mathbf{P}_2^{(3)}$ yields the conventional expression of $X^{(3)}$ which has been presented in Section III, we shall now study the effect of $\mathbf{P}_1^{(3)}$ on $X^{(3)}$. Notice that

$$\mathbf{P}_1^{(3)}=\{[\rho_{ab}^{(3)}(t)]_1\boldsymbol{\mu}_{ba}+[\rho_{ba}^{(3)}(t)]_1\boldsymbol{\mu}_{ab}\}+\{[\rho_{bc}^{(3)}(t)]_1\boldsymbol{\mu}_{cb}+[\rho_{cb}^{(3)}(t)]_1\boldsymbol{\mu}_{bc}\}+\{[\rho_{ca}^{(3)}(t)]_1\boldsymbol{\mu}_{ac}+[\rho_{ac}^{(3)}(t)]_1\boldsymbol{\mu}_{ca}\}\;, \tag{A5}$$

where all the required quantities have been developed before. For instance, $\rho_{ab}^{(3)}(t)_1$ can be written in the form

$$[\rho_{ab}^{(3)}(t)]_1=-\frac{1}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)[2\rho_{bb}^{(2)}(t_1)+\rho_{cc}^{(2)}(t_1)]\;, \tag{A6}$$

where $\rho_{bb}^{(2)}(t_1)$ and $\rho_{cc}^{(2)}(t_1)$ are given by Eqs. (2.29) and (2.30). Therefore $[\rho_{ab}^{(3)}(t)]_1$ can be written as

$$[\rho_{ab}^{(3)}(t)]_1=[\rho_{ab}^{(3)}(t)]_{1b}+[\rho_{ab}^{(3)}(t)]_{1c}\;, \tag{A7}$$

where

$$\begin{aligned}
[\rho_{ab}^{(3)}(t)]_{1b}&=-\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)\int_0^{t_1}dt_2\frac{f_b(t_1-t_2)}{\lambda_1-\lambda_2}[e^{-\lambda_2 t_2}(2c_c-2\lambda_2-c_b)+e^{-\lambda_1 t_2}(2\lambda_1-2c_c+c_b)]\;,\\
[\rho_{ab}^{(3)}(t)]_{1c}&=-\frac{i}{\hbar}\int_0^t dt_1 e^{i\omega'_{ab}(t_1-t)}H'_{ab}(t_1)\int_0^{t_1}dt_2\frac{f_c(t_1-t_2)}{\lambda_1-\lambda_2}[e^{-\lambda_2 t_2}(b_b-\lambda_2-2b_c)+e^{-\lambda_1 t_2}(\lambda_1-b_b+2b_c)]\;.
\end{aligned} \tag{A8}$$

Notice that the various functions and constants included in these expressions have been defined previously. Performing the double time integration, the quantities $[\rho_{ab}^{(3)}(t)]_{1b}$ and $[\rho_{ab}^{(3)}(t)]_{1c}$ are evaluated. Then, the polarization and the resulting third-order optical nonlinear susceptibilities can be obtained in a straightforward manner. In this appendix we are concerned with contributions to the nonlinear susceptibility $[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_1$ given by

$$[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_1=[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ab}+[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1bc}+[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ac}\;, \tag{A9}$$

where, for example, $[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ab}$ represents the contributions from $[\rho_{ab}^{(3)}(t)]_1$ and $[\rho_{ba}^{(3)}(t)]_1$ in Eq. (A5). It takes the form

$$\begin{aligned}
[X_{ijkl}^{(3)}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ab}=&\sum_m\sum_{\alpha,\beta,\gamma}\frac{(\rho_{mm}^0-\rho_{bb}^0)}{2\hbar^3(\lambda_1-\lambda_2)}(\mu_{ba}^{(i)}\mu_{ab}^{(j)}\mu_{mb}^{(k)}\mu_{bm}^{(l)})\left[\frac{1}{\omega'_{mb}-\omega_\alpha}+\frac{1}{\omega'_{bm}-\omega_\beta}\right]\\
&\times\left[\frac{2c_c-2\lambda_2-c_b}{[i(\omega_\alpha+\omega_\beta)-\lambda_2][\lambda_2+i(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ab})]}\right.\\
&\left.+\frac{2\lambda_1-2c_c+c_b}{[i(\omega_\alpha+\omega_\beta)-\lambda_1][\lambda_1+i(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ab})]}\right]\\
&+\sum_m\sum_{\alpha,\beta,\gamma}\frac{(\rho_{mm}^0-\rho_{cc}^0)}{2\hbar^3(\lambda_1-\lambda_2)}(\mu_{ba}^{(i)}\mu_{ab}^{(j)}\mu_{mc}^{(k)}\mu_{cm}^{(l)})\left[\frac{1}{\omega'_{mc}-\omega_\alpha}+\frac{1}{\omega'_{cm}-\omega_\beta}\right]\\
&\times\left[\frac{b_b-\lambda_2-2b_c}{[i(\omega_\alpha+\omega_\beta)-\lambda_2][\lambda_2+i(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ab})]}\right.\\
&\left.+\frac{\lambda_1-b_b+2b_c}{[i(\omega_\alpha+\omega_\beta)-\lambda_1][\lambda_1+i(\omega_\alpha+\omega_\beta+\omega_\gamma-\omega'_{ab})]}\right]+[a\leftrightarrow b]\;,
\end{aligned} \tag{A10}$$

where the symbol $[a \leftrightarrow b]$ means that the same quantity must be added but a and b must be inverted. In addition, the expressions for $[X^{(3)}_{ijkl}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1bc}$ and $[X^{(3)}_{ijkl}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ac}$ can be obtained similarly. It should be noted that to obtain $X^{(3)}$ for two-level systems we simply find the coefficients of $(\rho^0_{aa}-\rho^0_{bb})$ and $(\rho^0_{bb}-\rho^0_{aa})$ in $[X^{(3)}_{ijkl}(\omega_\alpha,\omega_\beta,\omega_\gamma)]_{1ab}$ by setting $c_b=0$, $c_c=0$, and $b_c=0$. In other words, to calculate $X^{(3)}$ by using a two-level model we ignore not only the contribution from $\mathbf{P}^{(3)}_2$, but also the contribution from the $(\rho^0_{bb}-\rho^0_{cc})$ and $(\rho^0_{aa}-\rho^0_{cc})$ to $\mathbf{P}^{(3)}_1$.

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