Effects of arbitrary relaxation and strong-field dressing of energy levels on nonlinear optical susceptibilities

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A nonlinear response theory of a quantum-mechanical system undergoing arbitrary relaxation and interacting with fields, some of which may be strong enough to saturate optical transitions, is developed. Explicit expressions for second-order and third-order susceptibilities are obtained. If the fields are weak, then these expressions show the existence of additional resonant contributions to $\chi^{(n)}$ which arise due to inelastic collisions. Various applications of these $\chi^{(n)}$'s to modulation spectroscopy, four-wave mixing, and pump-probe experiments are discussed. The general structure suggests how the additional resonances can be used to determine inelastic rates in a Doppler-broadened medium. For saturating fields, $\chi^{(n)}$'s become dependent on the intensity of such fields and can be formally obtained from weak-field $\chi^{(n)}$'s, provided proper identification of unperturbed eigenfunctions, eigenvalues, and relaxation times is made. Such intensity-dependent $\chi^{(n)}$'s have resonant denominators which lead to resonances at Rabi frequencies and submultiples of these frequencies, the widths of which are also dependent on the strength of the field. In the special cases intensity-dependent $\chi^{(1)}$ agrees with the work of Cohen-Tannoudji and co-workers.

I. INTRODUCTION

The third-order nonlinear susceptibility $\chi^{(3)}(\omega_1,\omega_2,\omega_3)$ is the key for the understanding of a very wide class of nonlinear phenomena[1-3] such as four-wave mixing, two-photon absorption, Raman scattering, etc. Expressions for $\chi^{(3)}$ in various special cases are well known. Some years back, Bloembergen *et al.* discussed the unusual results that one can get in four-wave mixing if the relaxation effects are properly taken into account in the calculation of third-order susceptibility.[3] The general expressions[2,3] presented by Bloembergen *et al.* and by Flytzanis include the relaxation effects arising from phase-changing collisions. However, they ignore the effect of state-changing or inelastic collisions. Inelastic collisions are known to be important in many cases such as in ruby. For example, the coherence between any two levels can be significantly affected by such collisions.[4] It is desirable to have the general structure of $\chi^{(3)}$ and other nonlinear susceptibilities which would be valid for a system undergoing both elastic and inelastic collisions.

It is also of considerable interest to find the structure of the intensity-dependent susceptibilities for cases when some of the optical transitions are strongly pumped. The susceptibilities will then probe the structure of a strongly pumped system. Such intensity-dependent susceptibilities can be used for studying saturation effects[5] in a variety of situations such as in four-wave mixing.

The purpose of this paper is twofold: (a) to develop the nonlinear-response theory assuming a general relaxation model so that population-changing collisions can be accounted for and (b) to obtain intensity-dependent nonlinear susceptibilities. We will in fact show that the expressions for susceptibilities obtained for the general relaxation model can be used to obtain intensity-dependent susceptibilities if the dressed-atom approximation[6] is made and if proper identification of various frequencies and eigenfunctions is made.

The population-changing collisions lead to additional terms in the susceptibilities which become resonant when certain combinations of applied frequencies vanish. The width of these additional resonances is determined by the inelastic collisions. The organization of this paper is as follows. In Sec. II, we present a Liouville operator formulation of the nonlinear-response theory for a system undergoing arbitrary relaxation. Such a formulation is applicable to classical and quantum, as well as to stochastic systems. A compact form for the nth-order susceptibility is given. In Sec. III, we show how the intensity-dependent susceptibilities for a strongly pumped system are to be computed and how the formulation and results of Sec. II can be used to get such susceptibilities. Subsequent sections examine $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$.

We present complete symmetrized results for $\chi^{(2)}$ and $\chi^{(3)}$. The structure of the additional terms in $\chi^{(2)}$ and $\chi^{(3)}$ is discussed. Such terms are important in the determination of inelastic collisional parameters. Explicit results for $\chi^{(2)}$ and $\chi^{(3)}$ for two-level and three-level systems are given. Characteristics of the intensity-dependent susceptibilities are also presented. Various applications of the general form of χ's are discussed.

II. LIOUVILLE OPERATOR FORMULATION OF THE NONLINEAR-RESPONSE THEORY FOR A SYSTEM UNDERGOING ARBITRARY RELAXATION

Consider a quantum-mechanical system undergoing relaxation and interacting with external fields. The density-matrix equation for such a system can be written as

$$\frac{\partial\rho}{\partial t}=L_0\rho-i[H_f(t),\rho] , \tag{2.1}$$

where $H_f(t)$ describes the effect of external fields which in general are time dependent. Before the application of the fields, the system is in an equilibrium state $\rho^{(0)}$ which is an eigenstate of L_0,

$$L_0\rho^{(0)}=0 . \tag{2.2}$$

The Liouville operator L_0 has a simple structure $-i[H_0, \ ]$ if the system is initially in thermal equilibrium. Here we incorporate the effect of relaxation in a very general manner and hence we use the following structure for L_0:

$$(L_0\rho)_{ij}=(-i\omega_{ij}\rho_{ij}-\Gamma_{ij}\rho_{ij})(1-\delta_{ij}) +\delta_{ij}\left[\sum_k\left[\gamma_{ik}\rho_{kk}-\gamma_{ki}\rho_{ii}\right]\right] . \tag{2.3}$$

Here the frequencies ω_{ij} are in general shifted due to the relaxation effects. The quantities γ_{ij} give the inelastic rates for making a transition from the state $|j\rangle$ to $|i\rangle$. Off-diagonal elements of the density matrix decay at the rate Γ_{ij}. These decay rates also include contributions Γ_{ij}^{ph} from phase-changing collisions,

$$\Gamma_{ij}=\Gamma_{ij}^{\text{ph}}+\tfrac{1}{2}\sum_k(\gamma_{ki}+\gamma_{kj}) . \tag{2.4}$$

This model of relaxation is different from the most popularly used model[2,3,7] with pumping terms λ_i,

$$(L_0\rho)_{ij}=-i\omega_{ij}\rho_{ij}-\Gamma_{ij}\rho_{ij}+\lambda_i\delta_{ij} \quad \forall i,j . \tag{2.5}$$

It must be borne in mind that spontaneous emission, in general, corresponds to the model (2.3) with $\gamma_{ij}=0$ if $E_i>E_j$. The general formulation presented below also allows the possibility of treating the nonlinear response of systems in general nonequilibrium steady states,[8] since the eigenstate of L_0 corresponding to zero eigenvalue need not be the thermal equilibrium state.

In the usual calculations of the nonlinear susceptibilities the eigenfunctions and eigenvalues of the Hamiltonian of the system are quite useful. Similarly, for the present problem eigenfunctions of L_0 will be quite important. Hence we give a brief discussion of the eigenfunctions of L_0. From (2.3) it is clear that

$$L_0\psi_{kl}=-i\Lambda_{kl}\psi_{kl} ,$$
$$\psi_{kl}=|k\rangle\langle l| , \quad \Lambda_{kl}=\omega_{kl}-i\Gamma_{kl}, \quad k\neq l . \tag{2.6}$$

Thus ψ_{kl} are the eigenfunctions (which are in fact operators in the original Hilbert space) in the Liouville space of the operator L_0. Another set of eigenfunctions of L_0 can be constructed using the projectors $\psi_{kk}=|k\rangle\langle k|$. Since

$$L_0\psi_{kk}=\sum_{l\neq k}\gamma_{lk}(\psi_{ll}-\psi_{kk}) \tag{2.7}$$

and hence we write the eigenvalue problem as

$$L_0\phi_k=\lambda_k\phi_k , \tag{2.8}$$

$$\phi_k=\sum_l\mu_{kl}\psi_{ll}, \quad \psi_{ll}=\sum_k\nu_{lk}\phi_k . \tag{2.9}$$

The eigenvalues λ_k and the expansion coefficients μ,ν can be obtained from the solution of the eigenvalue problem

$$S^{-1}RS=\Lambda, \quad R_{kl}=\gamma_{kl}(k\neq l), \quad R_{kk}=-\sum_{l\neq k}\gamma_{lk} ,$$
$$S_{kl}=\mu_{lk}, \quad (S^{-1})_{kl}=\nu_{lk} . \tag{2.10}$$

If $\chi^{(i)}$ are the left eigenfunctions (row vector) of R, then

$$\nu_{kl}=\chi_k^l , \tag{2.11}$$

where χ_k^l denotes the kth component of the eigenfunction χ_l. The eigenfunction $\chi^{(0)}$ corresponding to zero eigenvalue has the simple structure

$$\chi_1^{(0)}=\chi_2^{(0)}=\cdots=\chi_N^{(0)} . \tag{2.12}$$

This follows from the property of the R matrix

$$\sum_k R_{kl}=0 . \tag{2.13}$$

Having gotten the eigenfunctions of L_0, it is possible to obtain the structure of $f(L_0)Q$ where f denotes a function of L_0 and Q is any arbitrary operator. It is clear that

$$f(L_0)Q=\sum_{k\neq l}Q_{kl}f(L_0)|k\rangle\langle l|+\sum_k Q_{kk}f(L_0)|k\rangle\langle k|$$

which on using (2.6) and (2.9) reduces to

$$f(L_0)Q=\sum_{k\neq l}Q_{kl}f(-i\Lambda_{kl})|k\rangle\langle l|+\sum_{k,l}Q_{kk}\nu_{kl}f(L_0)\phi_l$$
$$=\sum_{k\neq l}Q_{kl}f(-i\Lambda_{kl})|k\rangle\langle l|+\sum_{k,l}Q_{kk}\nu_{kl}f(\lambda_l)\phi_l . \tag{2.14}$$

The contribution of the zero eigenvalue to (2.14) will be

$$\sum_k Q_{kk}\chi_k^{(0)}f(0)\phi_0=\chi^{(0)}\sum_k Q_{kk}f(0)\phi_0 ,$$

where (2.12) has been used. Thus the zero eigenvalue will lead to a contribution proportional to $\text{Tr}Q$. Thus if Q is an operator whose trace is zero, then we get the result

$$f(L_0)Q=\sum_{k\neq l}Q_{kl}f(-i\Lambda_{kl})|k\rangle\langle l|+\sum_{\substack{k,l\\ \lambda_l\neq 0}}Q_{kk}\nu_{kl}f(\lambda_l)\phi_l . \tag{2.15}$$

This result will be important in the evaluation of the nonlinear response which we will new calculate. On writing

$$\rho=\sum_{n=0}^{\infty}\rho^{(n)}(t), \quad L_f(t)=-i[H_f(t), \ ] \tag{2.16}$$

in Eq. (2.1), standard perturbative methods show that

$$\rho^{(n)}(t)=\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_{n-1}}e^{L_0(t-t_1)}L_f(t_1)e^{L_0(t_1-t_2)}L_f(t_2)\cdots e^{L_0(t_{n-1}-t_n)}L_f(t_n)e^{L_0t_n}\rho^{(0)} \tag{2.17}$$

which can be further reduced to

$$\rho^{(n)}(t)=\int_{0}^{\infty}dt_1\int_{-\infty}^{t-t_1}dt_2\cdots\int_{-\infty}^{t_{n-1}}e^{L_0t_1}L_f(t-t_1)e^{L_0(t-t_1-t_2)}\cdots e^{L_0(t_{n-1}-t_n)}L_f(t_n)e^{L_0t_n}\rho^{(0)} . \tag{2.18}$$

Equation (2.18) can be further simplified by writing

$$H_f(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\, e^{-i\omega t}H_f(\omega) ,$$
$$L_f(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\, e^{-i\omega t}L_f(\omega) \tag{2.19}$$

and by using (2.2) ($e^{L_0t}\rho^{(0)}=0$). We then find the result

$$\rho^{(n)}(t)=\left[\frac{i}{2\pi}\right]^n\int_{-\infty}^{+\infty}\cdots\int d\omega_1\cdots d\omega_n e^{-it(\omega_1+\omega_2+\cdots+\omega_n)}$$
$$\times\left[\sum_i\omega_i-iL_0\right]^{-1}L_f(\omega_1)\left[\sum_{i=2}^{n}\omega_i-iL_0\right]^{-1}L_f(\omega_2)\cdots(\omega_n-iL_0)^{-1}L_f(\omega_n)\rho^{(0)} . \tag{2.20}$$

In deriving (2.20) we have used the fact that eigenvalues of L_0 have a negative real part. The only complication which can arise is from the zero eigenvalue. However, we show that the zero eigenvalue of L_0 does not contribute to (2.20). The structure of the eigenvalues of the Liouville operator L_0 has already been examined. Note that the operator L_fB has the form $-i[H_f,B]$ and hence $\mathrm{Tr}L_fB=0$. Thus the condition for the validity of (2.15) is satisfied and it then follows from the structure of (2.20) that the zero eigenvalue of L_0 will not contribute to (2.20).

Using (2.20) the nth-order nonlinear response for the physical variable Q becomes

$$Q^{(n)}(t)=\mathrm{Tr}(\rho^{(n)}Q)$$
$$=\left[\frac{i}{2\pi}\right]^n\int_{-\infty}^{+\infty}\cdots\int d\{\omega_n\}\exp\left[-it\left[\sum_i\omega_i\right]\right]\mathrm{Tr}\left[Q\left[\sum_i\omega_i-iL_0\right]^{-1}\right.$$
$$\left.\times L_f(\omega_1)\left[\sum_{i=2}^{n}\omega_i-iL_0\right]^{-1}L_f(\omega_2)\cdots L_f(\omega_n)\rho^{(0)}\right] . \tag{2.21}$$

If H_f is linear in external fields, i.e.,

$$H_f(\omega)=-\sum_\alpha f_\alpha(\omega)\mathscr{S}_\alpha , \tag{2.22}$$

then

$$Q^{(n)}(t)=\sum\left[\frac{1}{2\pi}\right]^n\int_{-\infty}^{+\infty}\cdots\int d\{\omega_n\}\exp\left[-it\left[\sum_i\omega_i\right]\right]\chi^{(n)}_{Q\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)f_{\alpha_1}(\omega_1)\cdots f_{\alpha_n}(\omega_n) , \tag{2.23}$$

where

$$\chi^{(n)}_{Q\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)=\frac{(-i)^n}{n!}\mathrm{sym\,Tr}\left[Q\left[\sum_{i=1}^{n}\omega_i-iL_0\right]^{-1}L_{\alpha_1}\left[\sum_{i=2}^{n}\omega_i-iL_0\right]^{-1}L_{\alpha_2}\cdots L_{\alpha_n}\rho^{(0)}\right] ,$$
$$L_{\alpha_n}=-i[\mathscr{S}_{\alpha_n}, \,] . \tag{2.24}$$

Here "sym" has the usual meaning, namely that the sum on the right-hand side has to be symmetrized over all the permutations of the indices (ω_i,α_i).

For the dipole Hamiltonian $\mathscr{S}_\alpha=d^{(\alpha)}$, $f_\alpha=E_\alpha$, where $d^{(\alpha)}$ is the αth component of the dipole moment operator and E is the external electric field. Choosing for Q the dipole moment operator, the induced polarization becomes

$$\mathbf{P}_\alpha(t)=\sum\left[\frac{1}{2\pi}\right]^n\int_{-\infty}^{+\infty}\cdots\int d\{\omega_n\}\exp\left[-it\left[\sum_i\omega_i\right]\right]\chi^{(n)}_{\alpha\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)E_{\alpha_1}(\omega_1)\cdots E_{\alpha_n}(\omega_n) \tag{2.25}$$

$$\equiv\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\,\mathbf{P}_\alpha(\omega)e^{-i\omega t} \tag{2.26}$$

which implies that the Fourier component of the induced polarization is

$$\mathbf{P}_\alpha(\omega)=\sum\left[\frac{1}{2\pi}\right]^{n-1}\int_{-\infty}^{+\infty}\cdots\int d\{\omega_n\}\delta\left[\omega-\sum_i\omega_i\right]\chi^{(n)}_{\alpha\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)E_{\alpha_1}(\omega_1)\cdots E_{\alpha_n}(\omega_n)\,. \tag{2.27}$$

The nonlinear susceptibility $\chi^{(n)}_{\alpha\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)$ is given by

$$\chi^{(n)}_{\alpha\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n)=N\frac{(-i)^n}{n!}\mathrm{sym\,Tr}\left[d^\alpha\left[\sum_{i=1}^n\omega_i-iL_0\right]^{-1}L_{\alpha_1}\left[\sum_{i=2}^n\omega_i-iL_0\right]^{-1}L_{\alpha_2}\cdots\left[\omega_n-iL_0\right]^{-1}L_{\alpha_n}\rho^{(0)}\right], \tag{2.28}$$

where we have introduced the density of atoms to get the polarization per unit volume. The above expression can be simplified by using the explicit forms (2.6) and (2.8) of the eigenfunctions and eigenvalues of the Liouville operator L_0. In subsequent sections we consider the explicit form of (2.28) for various values of n. The form (2.28) is quite useful in deriving sum rules[9,10] for the nonlinear optical susceptibilities which can be obtained by writing

$$\left[\sum_i\omega_i-iL_0\right]^{-1}=\sum_{n=0}^{\infty}(iL_0)^n\frac{1}{\left[\sum_i\omega_i\right]^{n+1}}\,. \tag{2.29}$$

III. NONLINEAR-RESPONSE THEORY WITH SATURATING FIELDS

Our analysis of Sec. II was based on perturbation theory in powers of the applied fields. Such a perturbative analysis is generally valid if the typical detunings from atomic resonances are far bigger than the typical Rabi frequencies ($\sim\mathbf{d}\cdot\mathbf{E}/\hbar$) for the optical transitions. If the fields are tuned close to resonance and if the Rabi frequencies are comparable to the relaxation rates, then one has to go beyond the simple perturbative approach. The fields which are strong are to be treated to all orders. Remaining fields can still be considered perturbatively. Thus nth order means order with respect to the weak fields. In this section we develop nonlinear-response theory when some of the applied fields are strong. We will work in the dressed-state basis and make use of the dressed-atom approximation.

We write the total Hamiltonian of the system interacting with external fields as

$$H=H_0+V(t)+F(t)\,, \tag{3.1}$$

where $V(t)$ $[F(t)]$ represents the interaction with strong [weak] fields. Since the strong fields are used generally in resonant situations, one can make a rotating-wave approximation as far as $V(t)$ is concerned. It is then possible to make a canonical transformation such that

$$U_r^{-1}(t)[H_0+V(t)]U_r(t)=\tilde{H}_0\,, \tag{3.2}$$

where $\tilde{H}_0$ is static. The choice of U_r depends on the structure of the energy levels and the external strong fields. Under the canonical transformation the part $F(t)$ transforms to

$$\tilde{F}(t)=U_r^{-1}(t)F(t)U_r(t)\,. \tag{3.3}$$

The weak-fields part $\tilde{F}(t)$ now will have different frequency dependence than that of $F(t)$. Rewriting (2.1) as

$$\frac{\partial\rho}{\partial t}=-i[H_0,\rho]-i[V(t)+F(t),\rho]+L_R\rho\,, \tag{3.4}$$

where L_R is the relaxation part of $L_0\equiv L_R-i[H_0,]$, and using the canonical transformation, (3.4) transforms into

$$\frac{\partial\tilde\rho}{\partial t}=-i[\tilde{h},\tilde\rho]-i[\tilde{F}(t),\tilde\rho]+L_R\tilde\rho\,, \tag{3.5}$$

where

$$\tilde{h}=\tilde{H}_0+\text{contribution from the terms }(U_r,U_r^{-1})\,. \tag{3.6}$$

We will now work in a representation in which $\tilde{h}$ is diagonal,

$$S^{-1}\tilde{h}S=\beta,\ \ \tilde{h}\,|\beta_i\rangle=\beta_i\,|\beta_i\rangle\,. \tag{3.7}$$

The eigenstates $|\beta_i\rangle$ and the eigenvalues β_i depend on the strong external fields. These are essentially the dressed states of the system.[6] Note that the conventional dressed-state description[6] uses the quantized version of the external fields whereas we have treated the fields classically.[11] The eigenstates $|\beta_i\rangle$ are the superposition of the eigenstates of H_0 with expansion coefficients that depend on the strength of the strong field. We now transform (3.5) to the basis in which $\tilde{h}$ is diagonal. On defining

$$\underset{\sim}{\rho}=S^{-1}\tilde\rho S,\ \ \underset{\sim}{F}(t)=S^{-1}\tilde{F}(t)S\,, \tag{3.8}$$

Eq. (3.5) leads to

$$\frac{\partial\underset{\sim}{\rho}}{\partial t}=-i[\beta,\underset{\sim}{\rho}]-i[\underset{\sim}{F}(t),\underset{\sim}{\rho}]+S^{-1}[L_R(S\underset{\sim}{\rho}S^{-1})]S\,. \tag{3.9}$$

The relaxation terms now acquire a much more complicated form. The dressed-atom approximation[6,11] consists of using

$$\langle\beta_i\,|S^{-1}[L_R(S\underset{\sim}{\rho}S^{-1})]S\,|\beta_j\rangle\approx-q_{ij}\underset{\sim}{\rho}_{ij}(1-\delta_{ij})+\delta_{ij}\left[\sum_k p_{ik}\underset{\sim}{\rho}_{kk}-p_{ki}\underset{\sim}{\rho}_{ii}\right]\equiv(L_D\underset{\sim}{\rho})_{ij}\,. \tag{3.10}$$

Here q_{ij} and p_{ij} are the new relaxation parameters which are field dependent. Thus in the dressed-atom approximation (3.9) reduces to

$$\frac{\partial \underline{\rho}}{\partial t} = -i[\beta,\underline{\rho}] - i[\underline{F}(t),\underline{\rho}] + L_D\underline{\rho} \ . \tag{3.11}$$

We have thus proved that if we work in the dressed-state basis and if we use the dressed-atom approximation, then the basic dynamical equation (3.11) has the same structure as (2.1) which was used in perturbative calculations. Thus the density matrix $\underline{\rho}$ to nth order in terms of $\underline{F}(t)$ can be obtained from (2.20). The response of the observable Q can be written as

$$\begin{aligned} Q(t) &= \mathrm{Tr}[\rho(t)Q] = \mathrm{Tr}[U_r(t)\tilde{\rho}(t)U_r^{-1}(t)Q] \\ &= \mathrm{Tr}[\tilde{\rho}(t)\tilde{Q}(t)] = \mathrm{Tr}[S^{-1}\tilde{\rho}(t)\tilde{Q}(t)S] \\ &= \mathrm{Tr}[\underline{\rho}(t)\underline{Q}(t)] \ . \end{aligned} \tag{3.12}$$

Thus nth-order nonlinear response of the observable Q will be given by (2.21) with $Q \to \underline{Q}(t)$, $L_0 \to L_D - i[\beta,]$, and

$$-i[\underline{F}(t),] = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t} L_f(\omega) \ . \tag{3.13}$$

It should be borne in mind that the matrix elements of L_f depend on the strength of the strong external fields. Note that if we write

$$\underline{Q}(t) = \sum_a Q_a e^{-i\omega_a t}, \quad \underline{F}(\omega) = -\sum_\alpha f_\alpha(\omega)\mathscr{S}_\alpha \ , \tag{3.14}$$

then the nonlinear response follows from (2.23) and (2.24):

$$Q^{(n)}(t) = \sum \left[\frac{1}{2\pi}\right]^n \int_{-\infty}^{+\infty} \cdots \int d\{\omega_n\} \exp\left[-it\left[\omega_a + \sum_i \omega_i\right]\right] f_{\alpha_1}(\omega_1)\cdots f_{\alpha_n}(\omega_n)\chi^{(n)}_{a\,\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n) \ , \tag{3.15}$$

where

$$\chi^{(n)}_{a\,\alpha_1,\ldots,\alpha_n}(\omega_1,\ldots,\omega_n) = (-i)^n \frac{1}{n!} \mathrm{sym}\,\mathrm{Tr}\left[Q_a\left[\sum \omega_i - iL_0\right]^{-1} L_{\alpha_1}\left[\sum_{i=2}^{n}\omega_i - iL_0\right]^{-1} L_{\alpha_2}\cdots L_{\alpha_n}\underline{\rho}^0\right], \quad L_{\alpha_n} = -i[\mathscr{S}_{\alpha_n},] \ . \tag{3.16}$$

The nth-order susceptibility (3.16) is intensity dependent because the new Liouville operators L_0 and L_α [Eq. (3.13)] depend on the strength of the saturating fields. Thus we have this remarkable result: Intensity-dependent susceptibilities can be obtained from those derived for weak fields if the (1) unperturbed eigenstates and eigenvalues are replaced by the dressed states and dressed energies, (2) relaxation parameters Γ_{kl},γ_{kl} are replaced by field-dependent parameters q_{ij},p_{ij}, and (3) transformation (3.14) is kept in view. It should be remembered that the frequencies $\omega_1,\omega_2,\ldots$ in (3.15) are *not* the frequencies of the weak external field but that these involve the combinations of the weak-field and strong-field frequencies because of the transformation (3.3).

In order to understand the abstract formulation given above consider the interaction of a two-level system with two external fields of frequencies ω_1 and ω_2 and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. We assume that the field ω_1 is strong and that ω_2 is weak. Then various parts of the Hamiltonian are

$$\begin{aligned} H_0 &= \frac{\omega_0}{2}(|1\rangle\langle 1| - |2\rangle\langle 2|) \ , \\ V(t) &= G(|1\rangle\langle 2| e^{i\mathbf{k}_1\cdot\mathbf{r} - i\omega_1 t} + \text{c.c.}) \ , \\ F(t) &= g(|1\rangle\langle 2| e^{i\mathbf{k}_2\cdot\mathbf{r} - i\omega_2 t} + \text{c.c.}) \ . \end{aligned} \tag{3.17}$$

The phase factor $\mathbf{k}_1\cdot\mathbf{r}$ can be absorbed in the definition of the state $|1\rangle$ with the understanding that $\mathbf{k}_2$ will now stand for $\mathbf{k}_2 - \mathbf{k}_1$. The canonical transformation leads to

$$\begin{aligned} \tilde{h} &= \frac{\omega_0 - \omega_1}{2}(|1\rangle\langle 1| - |2\rangle\langle 2|) + G(|1\rangle\langle 2| + |2\rangle\langle 1|) \ , \\ \tilde{F}(t) &= g(|1\rangle\langle 2| e^{i(\omega_1 - \omega_2)t + i\mathbf{k}_2\cdot\mathbf{r}} + \text{c.c.}) \ . \end{aligned} \tag{3.18}$$

The matrix $\tilde{h}$ is easily diagonalized with the results

$$\begin{aligned} \beta_i &= \pm\left[\frac{\Delta^2}{4} + G^2\right]^{1/2} \equiv \pm\beta_0, \quad \Delta = \omega_0 - \omega_1 \ , \\ S &= \begin{bmatrix} N & \mu N \\ -\mu N & N \end{bmatrix} , \\ |\beta_1\rangle &= \begin{bmatrix} N \\ -\mu N \end{bmatrix}, \quad |\beta_2\rangle = \begin{bmatrix} \mu N \\ N \end{bmatrix} , \\ N^2(1+\mu^2) &= 1, \quad \mu = \left[\frac{\Delta}{2} - \beta_0\right] \Big/ G \ . \end{aligned} \tag{3.19}$$

Using (3.18) we see that

$$\begin{aligned} [\underline{F}(t)]_{\alpha\beta} &= gS^{-1}_{\alpha 1}S_{2\beta}e^{i(\omega_1-\omega_2)t + i\mathbf{k}_2\cdot\mathbf{r}} \\ &\quad + gS^{-1}_{\alpha 2}S_{1\beta}e^{-i(\omega_1-\omega_2)t - i\mathbf{k}_2\cdot\mathbf{r}} \ . \end{aligned} \tag{3.20}$$

The induced polarization $\mathbf{P}(t)$ will be

$$\mathbf{P}(t) = \mathbf{d}\,\mathrm{Tr}[\rho(|1\rangle\langle 2| + |2\rangle\langle 1|)] \tag{3.21}$$

which on restoring phase factors and using the canonical transformations, etc., becomes

$$\mathbf{P}(t) = \mathbf{d}e^{-i\mathbf{k}_1\cdot\mathbf{r} + i\omega_1 t}\sum_{\alpha,\beta} S^{-1}_{\alpha 1}S_{2\beta}[\underline{\rho}(t)]_{\beta\alpha} + \text{c.c.} \tag{3.22}$$

The relaxation terms (3.10) can be calculated by using (3.19) and these are found to be (cf. Ref. 6)

$$\begin{aligned} q_{12} &= N^4[\tfrac{1}{2}(\gamma_{12}+\gamma_{21})(1+4\mu^2+\mu^4) + \Gamma^{\mathrm{ph}}(1+\mu^4)] \ , \\ p_{12} &= N^4(\gamma_{21}\mu^4 + \gamma_{12} + 2\Gamma^{\mathrm{ph}}\mu^2) \ , \\ p_{21} &= N^4(\gamma_{21} + \gamma_{12}\mu^4 + 2\Gamma^{\mathrm{ph}}\mu^2) \ . \end{aligned} \tag{3.23}$$

Multilevel systems can be dealt with in an analogous manner. The equations for $\underline{\rho}$ for optical double resonance and Raman scattering can be found in Ref. 11.

Finally, note that the zeroth-order solution itself can be used to describe nonlinear phenomena in saturating fields. For example, consider the case of triple resonance where the system can go from the state $|1\rangle$ to $|4\rangle$ via the successive absorption of resonant photons of frequencies $\omega_1,\omega_2,\omega_3$, i.e.,

$$|1\rangle \xrightarrow{\omega_1} |2\rangle \xrightarrow{\omega_2} |3\rangle \xrightarrow{\omega_3} |4\rangle \ .$$

Each of these fields may be strong. The induced polarization at $\omega_1+\omega_2+\omega_3$ ($d_{14}\neq 0$) will be related to the density-matrix element ρ_{14}. Thus generation[12] at $\omega_1+\omega_2+\omega_3$ in presence of strong fields can be described by ρ_{14} which in terms of the dressed-state elements will be

$$(\underline{\rho})_{14}=\sum_{\alpha}(U_r S)_{1\alpha}(\underline{\rho})_{\alpha\alpha}(S^{-1}U_r^{-1})_{\alpha 4} \ , \tag{3.24}$$

where we have used the fact $(\underline{\rho})_{\alpha\beta}=0$ if $\alpha\neq\beta$. The population distribution in the dressed-state basis depends on p_{ij}'s which in turn depend on the intensities of the various fields. Note that various energy offset factors like $\omega_{ij}-\omega_\alpha$ are contained in p_{ij}'s and the matrix S.

IV. FIRST-ORDER RESPONSE—EFFECTS OF DRESSING THE ATOMIC STATES

We use the general structure (2.28) to examine the effect of damping on the linear-response function

$$\chi^{(1)}_{\alpha\beta}(\omega)=-\mathrm{Tr}\{d^\alpha(\omega-iL_0)^{-1}[d^\beta,\rho^{(0)}]\} \ . \tag{4.1}$$

Expression (4.1) can be simplified by using (2.15) and the property $\rho^{(0)}_{kl}=\rho^{(0)}_{kk}\delta_{kl}$. Calculations show that

$$\chi^{(1)}_{\alpha\beta}(\omega)=\sum_{k\neq l} d^\alpha_{lk}d^\beta_{kl}(\rho^{(0)}_{kk}-\rho^{(0)}_{ll})(\omega+i\Gamma_{kl}-\omega_{kl})^{-1} \ . \tag{4.2}$$

The first-order response function has the usual form but the frequency ω_{kl} is replaced by the complex frequency

$$\omega_{kl}\rightarrow\omega_{kl}-i\Gamma_{kl} \ . \tag{4.3}$$

Expression (4.2) also holds for systems with permanent dipole moments, although such terms do not contribute to the linear-response function. $\chi^{(1)}$ is thus essentially independent of the model of relaxation as it is determined from the relaxation of off-diagonal elements of the density matrix. Inelastic collisional rates are included in Γ_{kl}.

We next comment on the intensity-dependent χ for the case when some of the energy levels of the system are dressed by a strong external field. The linear response with respect to another weak field will probe the dressing of the states of the system. In place of (4.2) we will get from (3.16) the result

$$\chi^{(1)}_{\alpha\alpha}(\omega_1)=\sum_{k\neq l}(\underline{Q}_{\alpha})_{lk}(S_\alpha)_{kl}[(\underline{\rho}^{(0)})_{kk}-(\underline{\rho}^{(0)})_{ll}] \times(\omega_1+iq_{kl}-\beta_k+\beta_l)^{-1} \ , \tag{4.4}$$

where β_k's are the energies of the dressed states, q_{kl} is the intensity-dependent relaxation coefficient of the off-diagonal element of ρ in the dressed-state basis. For the special case of a two-level system driven by a strong field and by a weak field, the induced polarization can be obtained from (3.22). On combining (3.20) and (3.22) we find induced polarization to have contributions at ω_2 and at $2\omega_1-\omega_2$. The latter is just the four-wave-mixing contribution with saturation accounted for. We write polarization as

$$\mathbf{P}(t)=\mathbf{d}e^{-i\omega_2 t+i\mathbf{k}_2\cdot\mathbf{r}}p(\omega_2) +\mathbf{d}e^{-i(2\omega_1-\omega_2)t+i(2\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}}p(2\omega_1-\omega_2)+\mathrm{c.c.} \tag{4.5}$$

Explicit expressions for $p(\omega_1)$ and $p(2\omega_1-\omega_2)$ are found to be (cf. Refs. 6 and 13)

$$p(\omega_2)=\sum_{k\neq l}S^{-1*}_{l1}S^*_{2k}gS^{-1}_{k1}S_{2l}[-(\underline{\rho}^{(0)})_{kk}+(\underline{\rho}^{(0)})_{ll}] \times[(\omega_2-\omega_1)+iq_{kl}-\beta_k+\beta_l]^{-1} \ , \tag{4.6}$$

$$p(2\omega_1-\omega_2)=\sum_{k\neq l}S^{-1*}_{l1}S^*_{2k}gS^{-1}_{k2}S_{1l}[-(\underline{\rho}^{(0)})_{kk}+(\underline{\rho}^{(0)})_{ll}] \times[(\omega_1-\omega_2)+iq_{kl}-\beta_k+\beta_l]^{-1} \ . \tag{4.7}$$

These have resonances at $\omega_1-\omega_2=\pm 2\beta_0$ [β_0 defined by (3.19)] with a width q_{12}. Note that the resonance at Rabi frequency in nondegenerate four-wave mixing are now understood. The contribution (4.7) can also be used for studying the transfer of modulation[14] from a probe beam to a saturating beam. For this purpose assume that the probe beam has components $\omega_2,\omega_2\pm\Omega$. The total induced polarization will be obtained by summing over the contributions obtained from each probe frequency. For the special case $\omega_1=\omega_2$, the modulation transfer will be peaked[14] at $\Omega=\pm 2\beta_0$.

V. SECOND-ORDER RESPONSE

We calculate the explicit form of the second-order response function $\chi^{(2)}$. Here the model for relaxation can make substantial difference in the structure. From (2.28), the second-order response function $\chi^{(2)}$ is

$$\chi^{(2)}_{\alpha\beta\gamma}(\omega_1,\omega_2)=\frac{N}{2}\mathrm{sym}\,\mathrm{Tr}(d^\alpha(\omega_1+\omega_2-iL_0)^{-1} \times[d^\beta,\{(\omega_2-iL_0)^{-1}[d^\gamma,\rho_0]\}]) \tag{5.1}$$

which on using (2.15) reduces to

$$\chi^{(2)}_{\alpha\beta\gamma}(\omega_1,\omega_2) =\frac{N}{2}\mathrm{sym}\sum_{k\neq l}(\omega_2-\Lambda_{kl})^{-1}d^\gamma_{kl}[(\rho^{(0)})_{ll}-(\rho^{(0)})_{kk}] \times\mathrm{Tr}\{d^\alpha(\omega_1+\omega_2-iL_0)^{-1}[d^\beta,|k\rangle\langle l|]\} \ . \tag{5.2}$$

We will now work out (5.2) in detail so that the procedure becomes clear. The commutator in (5.2) can be written as

$$[d^{\beta},|k\rangle\langle l|]=\sum_m d^{\beta}_{mk}|m\rangle\langle l|-\sum_m d^{\beta}_{lm}|k\rangle\langle m| \tag{5.3}$$

which has both diagonal and off-diagonal elements. The action of $(\omega_1+\omega_2-iL_0)^{-1}$ is rather simple. On separating out the diagonal and off-diagonal elements in (5.3) we can simplify (5.2) to

$$\chi^{(2)}_{\alpha\beta\gamma}(\omega_1,\omega_2)=\frac{N}{2}\text{sym}\sum_{k\neq l}(\omega_2-\Lambda_{kl})^{-1}d^{\gamma}_{kl}[(\rho^{(0)})_{ll}-(\rho^{(0)})_{kk}]$$
$$\times\left[\sum_{l\neq m}d^{\beta}_{mk}d^{\alpha}_{lm}(\omega_1+\omega_2-\Lambda_{ml})^{-1}-\sum_{m\neq k}d^{\beta}_{lm}d^{\alpha}_{mk}(\omega_1+\omega_2-\Lambda_{km})^{-1}\right.$$
$$\left.+d^{\beta}_{lk}\text{Tr}[d^{\alpha}(\omega_1+\omega_2-iL_0)^{-1}(|l\rangle\langle l|-|k\rangle\langle k|)]\right]. \tag{5.4}$$

The remaining terms in (5.4) can be simplified using (2.15). One can write

$$(\omega-iL_0)^{-1}|l\rangle\langle l|=\sum_q|q\rangle\langle q|B_{lq}(\omega)\,,$$
$$B_{lq}(\omega)\equiv\sum_{\substack{p\\ \lambda_p\neq 0}}\nu_{lp}(\omega-i\lambda_p)^{-1}\mu_{pq}\,, \tag{5.5}$$

where μ's and ν's are defined by (2.9). For the decay model which assumes that a population from each level leaks out of the system at the rate Γ_{kk}, we will have a much simpler result

$$(\omega-iL_0)^{-1}|l\rangle\langle l|=(\omega+i\Gamma_{ll})^{-1}|l\rangle\langle l| \tag{5.6}$$

which amounts to using the replacement

$$B_{lq}(\omega)\to\delta_{lq}(\omega+i\Gamma_{ll})^{-1},\quad \lambda_l\equiv-\Gamma_{ll}\,. \tag{5.7}$$

In view of this it is useful to introduce an auxiliary function

$$C_{ql}(\omega)=B_{ql}(\omega)-\delta_{ql}(\omega+i\Gamma_{ll})^{-1} \tag{5.8}$$

so that $C_{ql}\to 0$ for the simple relaxation model (2.5). We next simplify (5.4) by adding and subtracting terms like $d^{\beta}_{mk}d^{\alpha}_{mm}(\omega_1+\omega_2-\Lambda_{mm})^{-1}$ so that the awkward restrictions on summations can be removed. Then on using (5.8), we get the result

$$\chi^{(2)}_{\alpha\beta\gamma}(\omega_1,\omega_2)=\frac{N}{2}\text{sym}\sum_{k,l}(\omega_2-\Lambda_{kl})^{-1}d^{\gamma}_{kl}[(\rho^{(0)})_{ll}-(\rho^{(0)})_{kk}]$$
$$\times\left[\sum_m d^{\beta}_{mk}d^{\alpha}_{lm}(\omega_1+\omega_2-\Lambda_{ml})^{-1}-d^{\beta}_{lm}d^{\alpha}_{mk}(\omega_1+\omega_2-\Lambda_{km})^{-1}\right.$$
$$\left.+d^{\beta}_{lk}d^{\alpha}_{mm}[C_{lm}(\omega_1+\omega_2)-C_{km}(\omega_1+\omega_2)]\right]. \tag{5.9}$$

We now give the complete symmetrized form of $\chi^{(2)}$. We adopt the notation[3] of Bloembergen *et al.* for writing the product of dipole matrix elements: $\mu\alpha\beta$ will stand for $d^{\mu}_{ik}d^{\alpha}_{kj}d^{\beta}_{ji}$. The symmetrized form is

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)=\frac{N}{2}\sum_{i,j,k}\rho^{(0)}_{ii}\left\{d_{ik}d_{kj}d_{ji}\left[\left[\frac{\mu\alpha\beta}{(\Lambda_{ji}-\omega_2)(\Lambda_{ki}-\omega_p)}+\frac{\beta\alpha\mu}{(\Lambda_{ij}-\omega_p)(\Lambda_{ik}-\omega_2)}\right.\right.\right.$$
$$\left.-\frac{\alpha\mu\beta}{(\Lambda_{jk}-\omega_p)(\Lambda_{ji}-\omega_2)}-\frac{\beta\mu\alpha}{(\Lambda_{jk}-\omega_p)(\Lambda_{ik}-\omega_2)}\right]$$
$$\left.+d^{\alpha}_{ik}d^{\beta}_{ki}d^{\mu}_{jj}\left[\frac{1}{\Lambda_{ik}-\omega_1}+\frac{1}{\Lambda_{ki}-\omega_2}\right][C_{kj}(\omega_p)-C_{ij}(\omega_p)]\right]$$
$$\left.+\begin{bmatrix}\alpha\\ \omega_1\end{bmatrix}\leftrightarrow\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}\right\},\quad \omega_p=\omega_1+\omega_2\,, \tag{5.10}$$

where ( )$\leftrightarrow$( ) indicates a permutation, interchanging the specified indices. Our expression (5.10) includes contributions from both elastic and inelastic collisions. The terms involving C's are new. If we let $C\to 0$, then we recover the result of Bloembergen *et al.* We next look at some applications.

In the special case of a two-level system, the eigenvalues λ can be calculated explicitly and we can get the following result for $\chi^{(2)}$:

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)=(\rho^{(0)}_{11}-\rho^{(0)}_{22})\frac{N}{2}\left\{(d^{\alpha}_{22}-d^{\alpha}_{11})\left[\frac{d^{\beta}_{12}d^{\mu}_{21}}{(\Lambda_{12}-\omega_p)(\Lambda_{12}-\omega_2)}+\frac{d^{\mu}_{12}d^{\beta}_{21}}{(\Lambda_{21}-\omega_p)(\Lambda_{21}-\omega_2)}\right]\right.$$
$$\left.+\frac{d^{\mu}_{22}-d^{\mu}_{11}}{i(\gamma_{12}+\gamma_{21})+\omega_p}\left[d^{\alpha}_{12}d^{\beta}_{21}\left[\frac{1}{\Lambda_{12}-\omega_1}+\frac{1}{\Lambda_{21}-\omega_2}\right]\right]+\begin{bmatrix}\alpha\\ \omega_1\end{bmatrix}\leftrightarrow\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}\right\}, \tag{5.11}$$

which is obviously nonzero if $\mathbf{d}_{11}\neq\mathbf{d}_{22}\neq 0$. In addition to various resonances at $\omega_{12}=\omega_1$, ω_2, ω_p, etc., the second-order susceptibility also has a resonance at $\omega_1+\omega_2=0$. This resonance has a width which is determined by the inelastic collisions in the system. Thus information on the inelastic rates can be obtained from the structure of the resonance at $\omega_1+\omega_2=0$. Our $\chi^{(2)}$ will be useful, for example, in studying the parametric fluorescence in a medium when collisional relaxation effects are important.

Application of second-order response to laser-excited fluorescence

The second-order response of other system variables is also of great interest. For example, fluorescence studies under laser excitation essentially require the knowledge of the populations of various excited states to second order in the external field. Using the formulation of Sec. II, the population N_i of the ith level in steady state will be

$$N_i=\sum_{\beta,\gamma}e^{-i(\omega_1+\omega_2)t}\mathcal{N}^{(2)}_{i\beta\gamma}(\omega_1,\omega_2)E_\beta(\omega_1)E_\gamma(\omega_2)\ , \tag{5.12}$$

where $\mathcal{N}^{(2)}_{i\beta\gamma}(\omega_1,\omega_2)$ can be obtained from (5.9) if we replace d^{α} by the operator $|i\rangle\langle i|$. Thus the second-order susceptibilities give not only the coherent polarization but also can be used to get populations and hence the fluorescence. In particular one can use these to get the results for the modulation spectroscopy. For example, the modulated fluorescence at Ω will be determined by

$$\mathcal{N}^{(2)}_{i\beta\gamma}(\omega+\Omega,-\omega),\ \ \mathcal{N}^{(2)}_{i\beta\gamma}(-(\omega-\Omega),\omega)\ .$$

From (5.10) or (5.11) it is clear that the inelastic collision terms resonate at $\Omega=0$ with a width that is determined by inelastic collisions. Other terms resonate when $\omega\pm\Omega$ equals the atomic frequencies ω_{kl}. Thus for the off-resonant case, the peak at $\Omega=0$ can be used to determine the inelastic collisional rates. In particular if the system is Doppler broadened, then in the Doppler limit, the resonance at $\Omega=0$ will dominate as it is unaffected by Doppler broadening whereas other resonances $\omega\pm\Omega=\omega_{kl}$ will lead to background contributions and hence the inelastic rates can be obtained from the resonance at zero modulation frequency. This general result is in agreement with the earlier calculations[15] that showed that T_1 can be determined for a Doppler-broadened two-level system by doing modulation spectroscopy.

The second-order response for the case when some of the energy levels are dressed by a strong radiation field can be obtained from (5.10) or from (5.11) by using the general principle of Sec. III.

VI. EFFECTS OF ELASTIC AND INELASTIC COLLISIONS ON THIRD-ORDER NONLINEAR RESPONSE

In this section we consider the general structure of third-order nonlinear susceptibilities which describe a very large number of physical phenomena such as Raman scattering and four-wave mixing. The effects of inelastic collisions are expected to be quite significant here. The third-order susceptibility can be obtained from (2.28) by the repeated application of (2.15) and (5.5). The calculations are quite lengthy and we quote the final result in the symmetrized form:

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)=\frac{N}{6}[B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)+C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)+D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)]\ . \tag{6.1}$$

Here $B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$ is given by

$$B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)=\sum_{i,n,k,j}\rho^{(0)}_{ii}d_{in}d_{nk}d_{kj}d_{ji}$$
$$\times\left\{\left[\frac{\mu\alpha\beta\gamma}{(-\omega_p+\Lambda_{ni})(\Lambda_{ji}-\omega_3)(\Lambda_{ki}-\omega_2-\omega_3)}-\frac{\alpha\beta\gamma\mu}{(-\omega_p+\Lambda_{ij})(\Lambda_{in}-\omega_1)(\Lambda_{ik}-\omega_1-\omega_2)}\right.\right.$$
$$-\frac{\alpha\mu\beta\gamma}{\Lambda_{kn}-\omega_p}\left[\frac{1}{(\Lambda_{ki}-\omega_2-\omega_3)(\Lambda_{ji}-\omega_3)}+\frac{1}{(\Lambda_{jn}-\omega_1-\omega_3)(\Lambda_{ji}-\omega_3)}+\frac{1}{(\Lambda_{jn}-\omega_1-\omega_3)(\Lambda_{in}-\omega_1)}\right]$$

$$+\frac{\alpha\beta\mu\gamma}{\Lambda_{jk}-\omega_p}\left[\frac{1}{(\Lambda_{jn}-\omega_1-\omega_3)(\Lambda_{in}-\omega_1)}+\frac{1}{(\Lambda_{ik}-\omega_1-\omega_2)(\Lambda_{in}-\omega_1)}+\frac{1}{(\Lambda_{jn}-\omega_1-\omega_3)(\Lambda_{ji}-\omega_3)}\right]\Bigg]$$

+terms obtained by using permutations

$$\begin{bmatrix}\alpha & \beta & \gamma\\ \omega_1 & \omega_2 & \omega_3\end{bmatrix}\to\begin{bmatrix}\alpha & \gamma & \beta\\ \omega_1 & \omega_3 & \omega_2\end{bmatrix},\begin{bmatrix}\beta & \alpha & \gamma\\ \omega_2 & \omega_1 & \omega_3\end{bmatrix},\begin{bmatrix}\beta & \gamma & \alpha\\ \omega_2 & \omega_3 & \omega_1\end{bmatrix},\begin{bmatrix}\gamma & \alpha & \beta\\ \omega_3 & \omega_1 & \omega_2\end{bmatrix},\begin{bmatrix}\gamma & \beta & \alpha\\ \omega_3 & \omega_2 & \omega_1\end{bmatrix}\Bigg\} . \tag{6.2}$$

Other contributions $C^{(3)}$ and $D^{(3)}$ are given by

$$C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$$

$$=\sum_{i,n,k,j}\rho_{ii}^{(0)}d_{kn}d_{nk}d_{ij}d_{ji}\left\{\frac{A(\omega_2+\omega_3)}{\Lambda_{nk}-\omega_p}\left[\mu\alpha\beta\gamma\left[\frac{1}{\Lambda_{ij}-\omega_2}+\frac{1}{\Lambda_{ji}-\omega_3}\right]+\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}\leftrightarrow\begin{bmatrix}\gamma\\ \omega_3\end{bmatrix}\right]\right.$$

$$\left.+\begin{bmatrix}\alpha\\ \omega_1\end{bmatrix}\leftrightarrow\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}+\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}\to\begin{bmatrix}\alpha\\ \omega_1\end{bmatrix}+\begin{bmatrix}\gamma\\ \omega_3\end{bmatrix}\to\begin{bmatrix}\beta\\ \omega_2\end{bmatrix}+\begin{bmatrix}\alpha\\ \omega_1\end{bmatrix}\to\begin{bmatrix}\gamma\\ \omega_3\end{bmatrix}\right\} , \tag{6.3}$$

$$A(\omega)=C_{jk}+C_{in}-C_{jn}-C_{ik} ,$$

$$D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$$

$$=\sum_{i,m,n,k}\rho_{mm}^{(0)}d_{mn}d_{nk}d_{km}d_{ii}$$

$$\times\left\{\alpha\beta\gamma\mu\left[\left[\frac{-C_{mi}(\omega_p)+C_{ni}(\omega_p)}{(\Lambda_{nm}-\omega_2-\omega_3)(\Lambda_{km}-\omega_3)}\right]_R-\frac{-C_{mi}(\omega_p)+C_{ki}(\omega_p)}{(\Lambda_{mk}-\omega_1-\omega_2)(\Lambda_{mn}-\omega_1)}\right.\right.$$

$$\left.\left.-\left[\frac{-C_{ni}(\omega_p)+C_{ki}(\omega_p)}{\Lambda_{kn}-\omega_1-\omega_3}\right]_{\text{add res}}\left[\frac{1}{\Lambda_{mn}-\omega_1}+\frac{1}{\Lambda_{km}-\omega_3}\right]\right]\right.$$

+five permutations

$$\begin{bmatrix}\alpha & \beta & \gamma\\ \omega_1 & \omega_2 & \omega_3\end{bmatrix}\to\begin{bmatrix}\alpha & \gamma & \beta\\ \omega_1 & \omega_3 & \omega_2\end{bmatrix},\begin{bmatrix}\beta & \alpha & \gamma\\ \omega_2 & \omega_1 & \omega_3\end{bmatrix},\begin{bmatrix}\beta & \gamma & \alpha\\ \omega_2 & \omega_3 & \omega_1\end{bmatrix},\begin{bmatrix}\gamma & \alpha & \beta\\ \omega_3 & \omega_1 & \omega_2\end{bmatrix},\begin{bmatrix}\gamma & \beta & \alpha\\ \omega_3 & \omega_2 & \omega_1\end{bmatrix}\Bigg\} . \tag{6.4}$$

This is the most general form of $\chi^{(3)}$ for a system undergoing relaxation described by the Eq. (2.3). All the terms involving $C_{\alpha\beta}(\omega)$ are new and these arise as a result of population changes in the system due to collisions and spontaneous emission. If we put $C_{\alpha\beta}(\omega)=0$, then the above expression reduces to $B^{(3)}$ which is just the result of Bloembergen *et al.* If the system has no permanent dipole moment, then the contribution $D^{(3)}$ vanishes. Thus the contribution $C^{(3)}$ is essentially due to inelastic collisions. In contrast to the contribution $B^{(3)}$, $C^{(3)}$ has resonances whenever $\omega_1+\omega_2=0$, the width of such Rayleigh-like terms being determined from the inelastic collisions; moreover, such Rayleigh-like terms also have the possibility of two intermediate states resonating with one of the applied frequencies. Terms like

$$(\Lambda_{jn}-\omega_1-\omega_2)^{-1}[(\Lambda_{in}-\omega_1)^{-1}+(\Lambda_{ji}-\omega_2)^{-1}]$$

in $B^{(3)}$ lead to the pressure-induced extra resonances[3,7,16] as discussed by Bloembergen *et al.* Note that such additional resonances also occur in $D^{(3)}$ (see, for example, the term with the "add res" subscript in $D^{(3)}$). Thus some type of extra resonance can arise due to inelastic collisions. Note also the Raman-like contributions in $D^{(3)}$—one such contribution is marked with a subscript R. We next consider some applications of the general expression (6.1).

A. Susceptibilities for modes and phase conjugation in two-photon media

In the special cases where only the transitions among few levels are important, above expressions simplify considerably. We give a few examples. We first consider the problem of phase conjugation in two-level systems when the system has a permanent dipole moment and when the two levels are connected by a two-photon transition (cf. Ref. 17). Calculations using (6.1) show that the relevant susceptibilities are

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(-\omega,\omega,\omega) = -2\frac{(\rho_{11}^{(0)}-\rho_{22}^{(0)})(d_{11}^{\alpha}-d_{22}^{\alpha})d_{12}^{\gamma}}{(\Lambda_{12}-2\omega)(\Lambda_{12}-\omega)} \times \left[\frac{(d_{11}^{\beta}-d_{22}^{\beta})d_{21}^{\mu}}{\Lambda_{12}-\omega}+\frac{(d_{11}^{\mu}-d_{22}^{\mu})d_{21}^{\beta}}{\omega+i(\gamma_{12}+\gamma_{21})}\right], \quad (6.5)$$

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega,\omega,-\omega) = -2\frac{(\rho_{11}^{(0)}-\rho_{22}^{(0)})(d_{11}^{\alpha}-d_{22}^{\alpha})d_{12}^{\beta}}{(\Lambda_{12}-2\omega)(\Lambda_{12}-\omega)} \times \left[\frac{(d_{11}^{\gamma}-d_{22}^{\gamma})d_{21}^{\mu}}{\Lambda_{12}-\omega}+\frac{(d_{11}^{\mu}-d_{22}^{\mu})d_{21}^{\gamma}}{\omega+i(\gamma_{12}+\gamma_{21})}\right],$$

$$\rho_{11}^{(0)}\gamma_{21}=\gamma_{12}\rho_{22}^{(0)} . \quad (6.6)$$

These susceptibilities appear as coefficients in propagation equations for the probe and conjugate waves. These susceptibilities will also be needed for the description of the basic modes of the two-photon media.[18,19]

B. Pump-probe experiments in ruby

We consider another example where inelastic collisions are important. Consider optical transitions[20] in ruby, which is essentially a three-level system. Expression (6.1) specialized to the case of a three-level system with $d_{12}\neq 0$, $d_{13}=d_{23}=0$, and on making the rotating-wave approximation, leads to the following expressions for the susceptibilities describing absorption from a probe in the presence of a pump beam and four-wave mixing:

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,-\omega_1,\omega_2)=\frac{\rho_{11}^{(0)}-\rho_{22}^{(0)}}{\Lambda_{12}-\omega_2}\left\{d_{12}^{\alpha}d_{21}^{\beta}d_{12}^{\gamma}d_{21}^{\mu}\left[C(0)\left[\frac{1}{\Lambda_{12}-\omega_1}+\frac{1}{\Lambda_{21}+\omega_1}\right]+C(\omega_2-\omega_1)\left[\frac{1}{\Lambda_{12}-\omega_2}+\frac{1}{\Lambda_{21}+\omega_1}\right]\right]\right\}, \quad (6.7)$$

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_1,-\omega_2)=\frac{2}{3!}C\frac{(\omega_1-\omega_2)(\rho_{11}^{(0)}-\rho_{22}^{(0)})d_{12}^{\alpha}d_{12}^{\beta}d_{21}^{\gamma}d_{21}^{\mu}}{\Lambda_{12}-(2\omega_1-\omega_2)}\left[\frac{1}{\Lambda_{12}-\omega_1}+\frac{1}{\Lambda_{21}+\omega_2}\right].$$

Here the phase-changing collisions enter through Λ_{12} and the inelastic collisions enter through $C(\omega)$,

$$C(\omega)=\frac{i(\gamma_{31}+2\gamma_{23})+2\omega}{(i\lambda_1-\omega)(i\lambda_2-\omega)} , \quad (6.8)$$

where the λ's are the roots of the quadratic equation

$$\lambda^2+(\gamma_{12}+\gamma_{21}+\gamma_{31}+\gamma_{23})\lambda +(\gamma_{23}\gamma_{12}+\gamma_{23}\gamma_{31}+\gamma_{12}\gamma_{31}+\gamma_{23}\gamma_{21})=0 \quad (6.9)$$

and thus λ's are determined by the transition rates γ_{ij}. The equilibrium populations also depend on γ's:

$$\rho_{11}^{(0)}-\rho_{22}^{(0)} =\gamma_{23}(\gamma_{12}-\gamma_{21}-\gamma_{31})/[\gamma_{12}\gamma_{31}+\gamma_{23}(\gamma_{12}+\gamma_{21}+\gamma_{31})] . \quad (6.10)$$

The transfer of the population from the ground state $|2\rangle$ to the excited state $|1\rangle$ is expected to be negligible and thus if we let $\gamma_{12}\to 0$, then

$$C(\omega)\to\frac{2}{\omega+i(\gamma_{21}+\gamma_{31})}+\frac{i\gamma_{31}}{[\omega+i(\gamma_{21}+\gamma_{31})](\omega+i\gamma_{23})} . \quad (6.11)$$

Thus pump-probe experiments will show a resonant structure at $\omega_2=\omega_1$ with widths determined by $\gamma_{21}+\gamma_{31}$ and by γ_{23}, i.e., by the total decay rate of the excited state $|1\rangle$ and of the state $|3\rangle$ to which the system can decay from $|1\rangle$ by inelastic collisions. Note that in a system like ruby one will have a very narrow resonance at $\omega_1=\omega_2$ with width γ_{23}.

C. Resonances at submultiples of Rabi frequency in strong-field experiments

Using the general scheme outlined in Sec. III, we can also look at the susceptibilities which are of third order in weak fields but which hold to all orders in some strong resonant field. Some general features of such susceptibilities can be easily seen. For example, consider a system driven by a strong field at ω_1 and a weak field at ω_2. Then $\chi^{(3)}(\omega_2,-\omega_2,\omega_2)$ will describe energy absorption, from ω_2, to fourth order in the weak field. Let the strong field saturate the optical transition $|1\rangle\leftrightarrow|2\rangle$. Then in (6.1), we have to replace ω_2 by $\omega_2-\omega_1$ and Λ_{jn} by the dressed-state energies β_{jn}. It is clear from the structure of (6.1) that such an intensity-dependent susceptibility will not only have resonant structure when $\omega_2-\omega_1$ is equal to the Rabi frequency but also at the subharmonic of the Rabi frequency. For example, resonances like $\Lambda_{jn}=\omega_1+\omega_3$ will lead to $\beta_{jn}=2(\omega_2-\omega_1)$ and thus to a structure at half of the Rabi frequency. Such subharmonic resonances in the intensity-dependent susceptibilities have been extensively studied[21] recently.

Thus in conclusion we have derived general expressions for the nonlinear susceptibilities that completely take into account population-changing relaxations and the optical saturation effects. The structure of the resonances in these susceptibilities is discussed. Multiphoton resonances in the usual susceptibilities imply the existence of resonances at various submultiples of Rabi frequencies. Other applications of the results of this paper will be considered elsewhere.[22,23]

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