:OLLISION-INDUCED NONLINEAR OPTICAL PHENOMENA AND .L—ORDER NONLINEAR SUSCEPTIBILITIES IN STRONG FIELDS

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This is to certify that I, M.Sanjay Kumar, have carried out the research embodied in the present thesis for the full period prescribed under the Ph.D ordinances of the University.

I declare, to the best of my knowledge, that no part of this thesis was earlier submitted for the award of a research degree of any University.

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ABSTRACT

A nonlinear response theory of a quantum-mechanical system undergoing arbitrary relaxation and interacting with fields is developed. Explicit expressions for the susceptibilities to second and third order in the weak fields are obtained for a system undergoing both phase-changing as well as inelastic collisions. These expressions show the existence of additional resonant contributions to the nonlinear susceptibilities which arise both due to elastic and inelastic collisions. Various applications of these nonlinear susceptibilities 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.

The existing diagrammatic method of calculation of the nonlinear susceptibilities is generalized to obtain the contributions to these susceptibilities which arise due to inelastic collisions. The diagrams that yield all the terms in the second-order susceptibility and also the inelastic contributions to the third-order susceptibility are explicitly written down.

The theory of nonlinear response is generalized so that it is valid under arbitrary initial conditions and for all time-scales of interest. Explicit expressions for the first, second and third-order susceptibilities are obtained, which determine the transient response of an initially-prepared system that is

undergoing phase-changing and inelastic collisions. These expressions explain the various transient phenomena like quantum beats, transient fluorescence, transient four-wave mixing, etc. These are also useful for the time-resolved, frequency-resolved spectroscopy. For a system initially in thermal equilibrium, the transient nonlinear susceptibilities can be calculated by the use of a prescription for modifying each term in the steady-state expression. New resonances are shown to occur in transient nonlinear wave mixing, which are characterized by linewidths determined essentially by the time duration of interaction between the system and the fields. These new resonances disappear in the long-time limit unless one includes collisions with a buffer gas. The characteristics of such transient resonances are explicitly discussed in the context of four-wave mixing in several conventionally used systems.

We next study the effect of crossrelaxation on the third-order nonlinear processes, namely, saturated absorption and four-wave mixing, within the context of a model four-level system consisting of two transitions coupled by inelastic collisions. Numerical results displaying changes in the resonant structures in the four-wave mixing signals for a range of collisional parameters are presented. Crossrelaxation is found to give rise to the line-mixing and line-narrowing phenomena. It is also found to affect the collision-induced structures.

We develop the nonlinear response theory that is valid when some of the applied fields are strong while the others are weak. The casting of the dynamical equations in the dressed-state representation and the use of the dressed-atom approximation enables us to obtain the intensity-dependent susceptibilities to various orders in the weak fields by doing a simple renormalization of the various parameters that occur in the corresponding bare-atom expressions. The expression for the first - order intensity-dependent susceptibility for a two-level atom exhibits the resonances at the Rabi frequency of the strong field. It also explains the transfer of modulation from a weak probe to a strong pump. The higher-order intensity-dependent susceptibilities in the context of the two-level system are discussed and the occurence of the resonances at the various submultiples of the Rabi frequency are explained.

We also give a dressed-atom formulation of the nonlinear response which is valid under arbitrary initial conditions and for all time-scales of interest. An explicit expression for the linear transient response of a dressed system is obtained. This expression clearly shows the existence of the new transient resonances which have linewidths determined essentially by the interaction time. Our result also explains the recently observed transient suppression of the Autler-Townes doublet, under conditions when the system is initially prepared in a pure dressed state.

We use the dressed-atom formulation of nonlinear response theory to study the effects of crossrelaxation on the saturated absorption and four-wave mixing signals, in the context of a model four-level system, under conditions when the pump is strong. Our analytical results show the mixing and narrowing of the lines in the strong-field spectra.

In the last chapter we calculate various two-time correlation functions which are important in determining the spectral properties of the generated fields as well as the quantum-mechanical fluctuations in these fields. We give explicit expressions for the two-time correlation functions of the dipole moment operator to second order in the applied fields. These are valid for a system undergoing phase-changing and inelastic collisions. In the context of the two-level system we study the effect of collisions on the various correlation functions of the dipole moment operator. Both perturbative and non-perturbative expressions are given.

INTRODUCTION

The physical phenomena that arise due to the interaction of matter with radiation can be described in terms of the induced dipole moment $\vec{P}$. The magnitude of $\vec{P}$ depends on the strength of the external fields. If the strength of the external field $\vec{E}$ is much less than the strength of the atomic field $\vec{E}_m$ inside the medium, i.e., $|\vec{E}|/|\vec{E}_m| \ll 1$, then one can expand $\vec{P}$ in various powers of $\vec{E}$.

$$\vec{P} = \vec{P}_o + \overleftrightarrow{\chi}^{(1)} \cdot \vec{E} + \overleftrightarrow{\chi}^{(2)} : \vec{E}\,\vec{E} + \overleftrightarrow{\chi}^{(3)} : \vec{E}\,\vec{E}\,\vec{E} + \ldots , \qquad (1.1)$$

where $\vec{P}_o$ is the polarization inside the medium in the absence of the external fields and $\overleftrightarrow{\chi}^{(1)}$, $\overleftrightarrow{\chi}^{(2)}$, $\overleftrightarrow{\chi}^{(3)}$, ... are respectively the linear, second order, third-order,... susceptibility tensors of rank two, three, four and so on. Note that the induced polarization as given by (1.1) acts as a source term in the Maxwell's equations

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = - \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \vec{P} \qquad (1.2)$$

Equations (1.1) and (1.2) enable us to determine the fields inside a medium in a self-consistent fashion. Most optical phenomena can be described in terms of the induced polarization $\vec{P}$. For a given medium, $\vec{P}$ can be calculated in various ways. For instance, considering the medium to be a bunch of harmonic oscillators one can obtain an expression for $\vec{P}$. Drude and Lorentz[1] had first used such an oscillator model to describe the linear optical phenomena.

Many aspects of nonlinear optical phenomena can be understood in terms of the susceptibilities $\overleftrightarrow{\chi}^{(2)}$, $\overleftrightarrow{\chi}^{(3)}$ etc., calculated using oscillator models.[2] However, a rigorous theory of nonlinear response of atomic systems to external fields should necessarily involve a quantum mechanical description of the system. A quantum mechanical calculation of the nonlinear susceptibilities for a multilevel system was first presented by Armstrong et al.[3] Such a calculation essentially involves the solution of the density matrix equations of the system in presence of external fields. The mean value of the induced polarization is determined from the relation

$$\vec{P}(t) = Tr \left\{ \rho(t) \vec{d} \right\} \qquad (1.3)$$

where ρ is the density matrix of the system and $\vec{d}$ is the dipole moment operator. The n^{th} order susceptibility tensor is related to $\vec{P}(t)$ by the following relation

$$\vec{P}^{(n)}(t) = \int_{-\infty}^{\infty} dt_1 \ldots \int_{-\infty}^{\infty} dt_n \overleftrightarrow{\chi}^{(n)}(t-t_1, t_1-t_2, \ldots, t_{n-1}-t_n) \vdots$$

$$\vec{E}(t_1) \vec{E}(t_2) \ldots \vec{E}(t_n) \qquad (1.4)$$

The quantity of interest generally is the Fourier transform of the susceptibility tensor $\overleftrightarrow{\chi}^{(n)}$ appearing in the integrand in Eq. (1.4). The expressions for the nonlinear susceptibilities account for many features of the well-known nonlinear optical phenomena such as second-harmonic generation, two-photon absorption, etc.

However, the early results did not take relaxation into account in a rigorous way. Damping was introduced a posteriori by replacing the atomic frequencies ω_{ij} in the expressions for the susceptibilities by the complex atomic frequencies $\omega_{ij}-i\Gamma_{ij}$, where Γ_{ij} are the phenomenological damping parameters.[4] Bloembergan et al[5,6] were the first to treat relaxation in a systematic way in the calculation of the nonlinear susceptibilities. Using a relaxation model which included phase changing collisions, they showed that certain additional resonances occur in the susceptibility describing four-wave mixing. Such additional resonances vanish in the absence of collisions.[7] The work of Bloembergen et al led to a lot of activity[7,8] in the area of collisional effects on nonlinear optical phenomena. The pressure-induced extra resonances (PIER) were later found to occur in fluorescence[9,10] and absorption spectroscopy[11] as well. In recent years, it has been observed that collisions significantly enhance certain nonlinnear optical effects such as optical Faraday rotation[12] and optical field-induced circular birefringence.[13] Further, collisions have been shown to give rise to a self-focussing or self-defocussing of a nearly-resonant cw laser beam transmitted through a sodium cell.[14] All these phenomena can be understood in terms of the nonlinear susceptibilities derived by Bloembergen et al.[5] However, the relaxation model of Bloembergen et al is not general enough in that it does not take into account the inelastic or population-changing collisions. Inelastic collisions are known to be important in many systems such as ruby. Further it has also been observed that inelastic collisions that take the population out of

the relevant levels of the system too give rise to an extra resonance in four-wave mixing in a two-level system.[15] Thus, it is desirable to have the structure of the nonlinear susceptibilities which would be valid for a system undergoing inelastic collisions.

Just as collisions, the presence of a strong pump too has been known to give rise to very interesting effects in nonlinear optical phenomena.[16-19] Many new and interesting features have been shown to arise in the four-wave mixing spectra[16] and also in the spontaneous and stimulated Raman spectra[17], as the strength of the pump is increased. Further, in recent years, it has been observed that additional resonant structures arise in the absorption and four-wave mixing signals in presence of an intense pump as the strength of the probe field is increased more and more.[18] Besides, the combined effects of collisions and of pump saturation on nonlinear optical phenomena too are interesting. For example, collisions lead to spectral hole- burning[19,20] in homogeneous probe line shapes in presence of a strong pump. In situations such as above, the pump needs to be treated exactly; the perturbative expression as in (1.1) will not suffice as far as the pump is concerned. Thus it is desirable to have the structure of the intensity-dependent nonlinear susceptibilities which describe the nonlinear optical phenomena in presence of strong pumps as well as collisions.

A description of the nonlinear optical phenomena in terms of the mean value of the induced polarization $\vec{P}$ suffices for the study of a whole host of macroscopic phenomena like second harmonic generation, four-wave mixing, Raman scattering, etc. There are however situations where the knowledge of the induced polarization is not enough. In phenomena like resonance fluorescence[21] and squeezing,[22] the quantum mechanical fluctuations in the generated fields are important. Such fluctuations are in general determined in terms of a heirarchy of correlation functions of the electric field operator.[23] However, for many physical phenomena, it is enough to know the two-time correlation functions. For example, the power spectrum of the light scattered from an atomic system is related to the two-time correlation function $\langle E^{-}(t)\ E^{+}(t')\rangle$, where $E^{\pm}$ refer to the positive and negative frequency parts of the electric field operator $\vec{E}$. In phenomena such as squeezing, the so-called anomolous correlator[24] $\langle E^{+}(t)E^{+}(t')\rangle$ is important. As a consequence of (1.2), the electric field operator $\vec{E}$ will be related to the dipole moment operator $\vec{p}$. Thus the quantum mechanical fluctuations in the generated fields essentially depend on the fluctuations in the induced polarization $\vec{P}$. Hence it is important to know the two-time correlation functions such as $\langle p^{-}(t)p^{+}(t')\rangle$, $\langle p^{+}(t)p^{+}(t')\rangle$, etc., where $p^{\pm}$ refer to the positive and negative frequency parts of the dipole moment operator $\vec{p}$. Note, for instance, that $\langle p^{-}(t)p^{+}(t')\rangle \neq \langle p^{-}(t)\rangle\langle p^{+}(t')\rangle$ in general. The non-factorizability of such two-time correlation functions (and in general the multi-time correlation functions) is basically due to the fluctuations. The fluctua-

tions in the induced polarization arise essentially due to the stochastic nature of the interaction between the radiating atomic system and the heat bath. The heat bath, in the case of atomic vapors for instance, correspands to the collisions and to the zero point fluctuations that give rise to spontaneous emission. The fluctuations in the induced polarization brought about by the collisions for instance give rise to the redistribution[21,25] of the incident radiation. Further, the inelastic component in the resonance fluorescence spectrum[21] of a two-level atom in presence of a strong field is essentially due to the fluctuations in the induced polarization brought about by the zero-point fluctuations. The effect of such fluctuations on the anomalous correlator of scattered light too should be interesting. Thus, it is desirable to have the general structure of the two-time correlation functions in presence of collisions and in presence of strong fields.

The aim of this thesis is to develop a formulation of nonlinear response theory, taking into account in a unified way, the effects of arbitrary relaxation as well as the strong fields. In Chapter II, the nonlinear response theory of a quantum mechanical system coupled to a reservoir and interacting with external fields is developed. The treatment here is confined to the steady state regime. The applied fields are assumed to be weak so that they can be treated perturbatively. In the context of a relaxation model which includes phase-changing as well as inelastic collisions, explicit expressions for the first, second and third-order nonlinear susceptibilities are obtained. The second and third-order

susceptibilities show the existence not only of the usual pressure-induced extra resonances which arise due to phase-changing collisions, but also extra resonances which arise due to inelastic collisions.

Diagrammatic methods of calculation of the third-order susceptibilities have been very popular in the literature. Each term in the expression for the third-order susceptibility corresponds to a diagram and hence it is possible to interpret the contribution from each term to a particular process, in physical terms. Yee et al[26] calculated the third-order susceptibility taking into account the effect of damping (phase-changing collisions and the decay of level population out of the system) systematically by using double-sided Feynman diagrams. Prior[27] has written down diagrams corresponding to the forty eight terms that occur in the third-order susceptibility derived by Bloembergen et al.[5] In Chapter III, we generalize the diagramatic method of Yee et al and present diagrams corresponding to the additional contributions to the second and third-order susceptibilities coming from inelastic collisions.

In Chapter IV, the formulation of nonlinear response theory given in Chapter II is generalized so that it is valid not only for an arbitrary relaxation model but also under arbitrary initial conditions and for all time-scales of interest. General expressions for the first, second and third-order time-dependent susceptibilities are obtained. These explain the well-known beating phenomena

in fluorescence[28] absorption[29] and emission.[30] The general expression for $\chi^{(3)}$ can be used to obtain the transient probe absorption and transient four-wave mixing signals which are quite useful in time-resolved frequency-resolved spectroscopy.[31] Further, an examination of the various terms occuring in the general expression for the time-dependent third-order susceptibility leads us to predict that extra resonances do exist in four wave mixing (and in general in nonlinear wave mixing) even in the absence of collisions or field fluctuations. Chapter V is devoted to a detailed study of such resonances in the context of some model two and three-level systems. It is found that these transient extra resonances have linewidths determined essentially by the interaction time.

It is well-known that collisions not only bring about population changes among the various levels but they also give rise to a coupling (crossrelaxation) of closely-spaced transitions. In linear absorption, crossrelaxation is known to give rise to the mixing and narrowing of spectral lines with increasing pressure.[32] In Chapter VI, we generalize the relaxation model described in Chapter II and include terms which give rise to coherence-coherence and population-coherence coupling in the density matrix equations of motion of the system. Within the context of a model four-level system, the effect of crossrelaxation on the saturated absorption and four-wave mixing signals is examined. Apart from giving rise to the usual line-mixing and line-narrowing phenomena as in the linear absorption spectrum, crossrelaxation is found to

affect the collision-induced structures in these signals.

In Chater VII, we develop a version of the formulation of Chapter II that takes into account the effects of the strong fields. In the case when some of the fields are strong while others are weak, the casting of the dynamical equations in the dressed-state representation[33] and the use of the dressed-atom approximation enables us to obtain the intensity-dependent susceptibilities from the bare-atom susceptibilities by a simple re-identification (or renormalization) of the various parameters. The treatment in this chapter is confined to the steady-state case. The general expressions for the intensity-dependent susceptibilities show the existence of resonances at the frequencies corresponding to the transition frequencies of the dressed states. Thus for a two-level system, the intensity-dependent linear susceptibility exhibits a resonance at the Rabi frequency of the pump field. Within the context of the two-level model, the resonances at submultiples of the Rabi frequency arising in the second and third-order intensity-dependent susceptibilities are discussed.

In Chapter VIII, we develop a theory of the transient nonlinear response of an arbitrarily prepared system interacting with fields that could be intense. For the sake of illustration, the time-dependent intensity-dependent linear susceptibility in the case of a model three-level system is calculated. For a particular choice of the initial conditions, this susceptibility explains

clearly, for instance, the recently observed phenomena of the transient suppression of the Autler-Townes doublet in optical double resonance experiments.[34] Further, the time-dependent, intensity-dependent linear susceptibility for the two-level system is shown to exhibit an extra resonance which, if the dressed-atom approximation is made, exists only if the coherence between the two dressed states is non-zero. This extra resonance is shown to be the same as the transient extra resonance discussed in Chapter IV.

In Chapter IX, the effects of crossrelaxation in presence of strong fields are studied. In the context of the four-level model described in Chapter VI, the dressed-atom formulation of Chapter VII is used to obtain analytical results for the saturated absorption and four-wave mixing spectra. It is evident from the analytical expressions that the mixing and narrowing of lines due to crossrelaxation occurs in the strong-field spectra as well.

Finally in Chapter X, we show how the formalism of nonlinear optics can be generalized to study the fluctuation phenomena. Explicit expressions for the two-time correlation functions to second order in the exciting field are given which are valid for a system undergoing phase-changing and inelastic collisions. The effects of collisions on the fluorescence spectrum and the anomalous correlator of a two-level system excited by a weak field are discussed. We also show how the correlation functions in presence of strong exciting fields can be obtained using

the dressed-atom formulation of Chapter VII. We give explicit expressions for the correlation functions of a two-level atom excited by a strong field. Our results reduce, in special cases, to the well-known results.

CHAPTER II

EFFECTS OF ARBITRARY RELAXATION ON NONLINEAR OPTICAL SUSCEPTIBILITIES

A wide class of nonlinear phenomena[2,5,35] such as four-wave mixing, two photon absorption, Raman scattering etc., can be understood in terms of the third-order nonlinear susceptibility $\chi^{(3)}(\omega_1,\omega_2,\omega_3)$. The effects of collisions on such nonlinear phenomena can be best studied by examining how the collisions modify the structure of $\chi^{(3)}$. Bloembergen et al[5] were the first to show that if the relaxation is properly taken into account, then the four-wave mixing susceptibility, for instance, shows certain additional resonances which would vanish in the absence of collisions. The general expressions for nonlinear susceptibilities presented by Bloembergen et al and by Flytzanis[35] include the relaxation effects arising from phase-changing collisions. However they ignore inelastic or state-changing collisions. Inelastic collisions are known to be important in many cases such as in ruby. For instance, the coherence between any two-levels can be significantly affected by such collisions.[25,36] 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. In this Chapter, we develop a nonlinear response theory assuming a general relaxation model so that population-changing collisions can be accounted for. 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. In Section II, we present a Liouville operator formulation of the nonlinear response theory for a system undergoing arbitrary relaxation. A compact form of the n^{th} order susceptibility is given. We present complete symmetrized expressions for $\chi^{(2)}$ and $\chi^{(3)}$. The structure of additional terms in $\chi^{(2)}$ and $\chi^{(3)}$ is discussed. Such additional terms are important in the determination of inelastic collisional parameters.

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

$$\frac{\partial \rho}{\partial t} = L_o \rho - i[\, H_f(t) \;,\; \rho \,] \;, \qquad (2.1)$$

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 $\rho^{(o)}$ which is an eigenstate of L_o ;

$$L_o \rho^{(o)} = 0 \qquad (2.2)$$

the Liouville operator L_o has a simple structure $-i[H_o, \ ]$, 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_o:

$$(L_o\rho)_{ij} = (-i\omega_{ij}\rho_{ij} - \Gamma_{ij}\rho_{ij})(1-\delta_{ij}) + \delta_{ij}\sum_k (\gamma_{ik}\rho_{kk} - \gamma_{ki}\rho_{ii}) \tag{2.3}$$

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 $|i\rangle$. Note that γ_{ij} for $E_j > E_i$ includes spontaneous emission as well. Off-diagonal elements of the density matrix decay at the rate Γ_{ij}. These decay rates include contributions Γ_{ij}^{ph} from phase-changing collisions,

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

This model of relaxation is different from the most popularly used model[2,35,37] with pumping terms λ_i,

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

Hence the usual relaxation model (2.5) includes phase-changing collisions and the decay of population from each level $|i\rangle$ at the rate of Γ_{ii} out of the system. Thus (2.5) does not include spontaneous emission to the levels in the system but out of the system and the inelastic collisions. The general formulation presented

below also allows the possibility of treating the nonlinear response of systems in general non-equilibrium steady states[38] since the eigenstate of L_o corresponding to the 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_o will be quite important. Hence we give a brief discussion of the eigenfunctions of L_o. From (2.3) it is clear that

$$L_o\psi_{k\ell} = -i\Lambda_{k\ell}\psi_{k\ell}$$

$$\psi_{k\ell} = |k\rangle\langle\ell| \qquad \Lambda_{k\ell} = \omega_{k\ell} - i\Gamma_{k\ell} , \quad k \neq \ell . \qquad (2.6)$$

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

$$L_o\psi_{kk} = \sum_{\ell\neq k} \gamma_{\ell k} (\psi_{\ell\ell} - \psi_{kk}) , \qquad (2.7)$$

we write the eigenvalue problem as

$$L_o\phi_k = \lambda_k\phi_k , \qquad (2.8)$$

$$\phi_k = \sum_{\ell} \mu_{k\ell}\psi_{\ell\ell} \quad , \quad \psi_{\ell\ell} = \sum_{k} \nu_{\ell k}\phi_k \tag{2.9}$$

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

$$S^{-1}RS = \Lambda, \; R_{k\ell} = \gamma_{k\ell}(k\neq\ell), \; R_{kk} = -\sum_{\ell\neq k} \gamma_{\ell k} \quad ,$$

$$S_{k\ell} = \mu_{\ell k} \quad , \; (S^{-1})_{k\ell} = \nu_{\ell k} \tag{2.10}$$

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

$$\nu_{k\ell} = \chi_k^{\ell} \quad , \tag{2.11}$$

where χ_k^{ℓ} denotes the k^{th} component of the eigenfunction $\chi^{(\ell)}$. The eigenfunction $\chi^{(o)}$ corresponding to zero eigenvalue has the simple structure

$$\chi_1^o = \chi_2^o = \ldots = \chi_N^o \tag{2.12}$$

This follows from the property of the R matrix

$$\sum_{k} R_{k\ell} = 0 \tag{2.13}$$

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

$$f(L_o)Q = \sum_{k\neq\ell} Q_{k\ell} f(L_o)|k><\ell| + \sum_k Q_{kk} f(L_o)|k><k|$$

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

$$f(L_o)Q = \sum_{k\neq\ell} Q_{k\ell}\, f(-i\Lambda_{k\ell})|k><\ell| + \sum_{k,\ell} Q_{kk} v_{k\ell}\, f(L_o)\phi_\ell$$

$$= \sum_{k\neq\ell} Q_{k\ell} f(-i\Lambda_{k\ell})|k><\ell| + \sum_{k,\ell} Q_{kk} v_{k\ell} f(\lambda_\ell)\phi_\ell \quad . \qquad (2.14)$$

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

$$\sum_k Q_{kk} \chi_k^{(o)} f(o)\phi_o = \chi^{(o)} \sum_k Q_{kk} f(o)\phi_o \quad ,$$

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

$$f(L_o)Q = \sum_{k\neq\ell} Q_{k\ell} f(-i\Lambda_{k\ell})|k><\ell| + \sum_{\substack{k,\ell \\ \lambda_\ell \neq 0}} Q_{kk} v_{k\ell}\, f(\lambda_\ell)\phi_\ell \quad . \qquad (2.15)$$

This result will be important in the evaluation of the nonlinear response which we will now calculate. The equation of motion Eq.(2.1) can be written in the integral form as

$$\rho(t) = e^{L_o(t-t_o)}\, \rho(t_o) + \int_{t_o}^{t} dt_1\, e^{L_o(t-t_1)} L_f(t_1)\, \rho(t_1) \quad , \qquad (2.16)$$

where we have defined

$$L_f(t) = -i\,[H_f(t)\,,\,] \qquad (2.17)$$

Here t_o refers to the time of application of the fields. Iterating Eq.(2.16) successively ad infinitum, we get a solution for $\rho(t)$

$$\rho(t) = \sum_{n=o}^{\infty} \left\{ \int_{t_o}^{t} dt_1 \ldots \int_{t_o}^{t_{n-1}} dt_n\, e^{L_o(t-t_1)} L_f(t_1)\, e^{L_o(t_1-t_2)} L_f(t_2) \right.$$

$$\left. \ldots\, e^{L_o(t_{n-1}-t_n)}\, L_f(t_n)\, e^{L_o(t_n-t_o)}\, \rho(t_o) \right\} . \qquad (2.18)$$

If we are interested in the steady state response of a system that is initially in thermal equilibrium, then we can replace $e^{L_o(t_n-t_o)}\rho(t_o)$ in Eq.(2.18) by $\rho^{(o)}$ [as a consequence of Eq.(2.2)] and the lower limit in the integrals can be extended to $-\infty$. Standard perturbation theory consists of writing

$$\rho(t) = \sum_{n=o}^{\infty} \rho^{(n)}(t) \quad , \qquad (2.19)$$

where $\rho^{(n)}(t)$ corresponds to the density matrix to n^{th} order in the interaction $L_f(t)$ [Eq.(2.17)]. It follows from (2.18) and (2.19) that

$$\rho^{(n)}(t) = \int_{-\infty}^{t} dt_1 \ldots \int_{-\infty}^{t_{n-1}} dt_n\, e^{L_o(t-t_1)} L_f(t_1)\, e^{L_o(t_1-t} L_f(t_2)$$

$$\ldots e^{L_o(t_{n-1}-t_n)} L_f(t_n)\, \rho^{(o)} \quad . \qquad (2.20)$$

The time integrals in Eq.(2.20) can be easily evaluted if one introduces the Fourier representations

$$H_f(t_l) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega_l\, e^{-i\omega_l t_l} H_f(\omega_l)$$

$$L_f(t_l) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega_l\, e^{-i\omega_l t_l} L_f(\omega_l) \qquad (2.21)$$

Note that the contribution from the lower limit of the time integrals vanishes as a result of the fact that the eigenvalues of L_o have a negative real part. Thus we obtain the simpler result

$$\rho^{(n)}(t) = (\frac{1}{2\pi})^n \int_{-\infty}^{\infty} \ldots \int d\omega_1 \ldots d\omega_n\, e^{-it(\omega_1+\omega_2+\ldots+\omega_n)}$$

$$\times \Big(\sum_{l=1}^{n} \omega_l - iL_o\Big)^{-1} L_f(\omega_1) \Big(\sum_{l=2}^{n} \omega_l - iL_o\Big)^{-1} L_f(\omega_2)$$

$$\ldots(\omega_n - iL_o)^{-1} L_f(\omega_n)\, \rho^{(o)} \qquad (2.22)$$

A complication can arise due to the zero eigenvalue of L_o; it can cause the expression in Eq.(2.22) to blow up when some combination of the ω_l's vanishes. However, we show that the zero eigenvalue of L_o does not contribute to (2.22). Note that the operator $L_f B$ has the form $-i[H_f,B]$ and hence Tr $L_f B=0$. Thus the condition for the validity of (2.15) is satisfied and it then follows from the structure of (2.22) that the zero eigenvalue of L_o will not contribute to (2.22). Using (2.22) the n^{th} order nonlinear response for the physical variable Q becomes

$$Q^{(n)}(t) = Tr(\rho^{(n)}(t)Q)$$

$$= \left(\frac{1}{2\pi}\right)^n \int_{-\infty}^{\infty} \cdots \int d\{\omega_n\}\, e^{-it\sum_l \omega_l} Tr\left\{Q\left(\sum_l \omega_l - iL_o\right)^{-1}\right.$$

$$\left. \times L_f(\omega_1)\left(\sum_{l=2}^{n}\omega_l - iL_o\right)^{-1} L_f(\omega_2)\cdots L_f(\omega_n)\,\rho^{(o)}\right\} \qquad (2.23)$$

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

$$H_f(\omega) = -\sum_\alpha f_\alpha(\omega)\, s_\alpha \quad , \qquad (2.24)$$

then

$$Q^{(n)}(t) = \sum\nolimits_{-} \left(\frac{1}{2\pi}\right)^n \int_{-\infty}^{\infty} \cdots \int d\{\omega_n\}\, e^{-it\sum_l \omega_l}$$

$$\times\ \chi^{(n}_{Q\{\alpha_n\}}(\{\omega_n\})\, f_{\alpha_1}(\omega_1)\cdots f_{\alpha_n}(\omega_n) \quad , \qquad (2.25)$$

where

$$\chi^{(n}_{Q\{\alpha_n\}}(\{\omega_n\}) = \frac{(-i)^n}{n!}\, sym\ Tr\left\{ Q\left(\sum\nolimits_{-}^{n} \omega_l - iL_o\right)^{-1}\right.$$

$$\left. L_{\alpha_1}\left(\sum\nolimits_{-}^{n}{}_{l=2} \omega_l - iL_o\right)^{-1} L_{\alpha_2}\cdots L_{\alpha_n}\rho^{(o)}\right\} \quad , \quad L_{\alpha_n} = -i[s_{\alpha_n}, \ ] \quad . (2.26)$$

Note that in (2.21), we have assigned the Fourier variable ω_l with the time variable t_l. Since the variables are time-ordered [Eq. (2.20)], i.e., $t_1 > t_2 > \ldots > t_n$, one can consider the expression in Eq.(2.23) to be the contribution to the nonlinear response $Q^{(n)}(t)$ coming from the fields $\omega_1, \omega_2, \ldots \omega_n$ acting on the system

in the above time order. However, since the assignment of the variables ω_i to the variables t_i above was quite arbitrary, it follows that the nonlinear response $Q^{(n)}(t)$ should consist of contributions coming from all possible time orders in which the fields $\omega_i, i=1,\ldots,n$ are acting on the system. We have taken care of this fact in Eqs.(2.25) and (2.26) by symmetrizing the usual expression. Thus, 'sym' in Eq.(2.26) means that the sum on the right-hand side has to be symmetrized over all permutations of the indices (ω_i,α_i). For the dipole Hamiltonian we have $s_\alpha = d^\alpha$, $f_\alpha = E_\alpha$, where d^α is the α^{th} component of the dipole moment operator and $\vec{E}$ is the external electric field. Choosing for Q the dipole moment operator, the induced polarization becomes

$$P_\alpha(t) = \sum_{-} \left(\frac{1}{2\pi}\right)^n \int_{-\infty}^{\infty} \ldots \int d[\omega_n]\, e^{-it\sum_i \omega_i}\, \chi^{(n}_{\alpha\{\alpha_n\}}(\{\omega_n\})$$

$$\times\ E_{\alpha_1}(\omega_1)\ldots E_{\alpha_n}(\omega_n) \qquad (2.27)$$

$$\equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, P_\alpha(\omega)\, e^{-i\omega t} \qquad (2.28)$$

which implies that the Fourier component of the induced polarization is

$$P_\alpha(t) = \sum_{-} \left(\frac{1}{2\pi}\right)^{n-1} \int_{-\infty}^{\infty} \ldots \int d[\omega_n]\, \delta(\omega-\textstyle\sum_i \omega_i)\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\})$$

$$\times\ E_{\alpha_1}(\omega_1)\ldots E_{\alpha_n}(\omega_n) \qquad (2.29)$$

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

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}) = N\frac{(-1)^n}{n!}\,\mathrm{sym\ Tr}\Big\{ d^{\alpha}\Big[\sum_{i=1}^{n}\omega_i - iL_o\Big]^{-1} \times L_{\alpha_1}\Big[\sum_{i=2}^{n}\omega_i - L_o\Big]^{-1} L_{\alpha_2}\cdots(\omega_n - iL_o)^{-1} L_{\alpha_n}\rho^{(o)}\Big\} ,$$

$$L_{\alpha} \equiv -i\,[d^{\alpha}, \quad] , \tag{2.30}$$

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 (2.5) and (2.7) of the eigenfunctions and eigenvalues of the Liouville operator L_o. More specifically, we write

$$\rho^{(o)} = \sum_{i} \rho^{(o)}_{ii}\,|i\rangle\langle i| \tag{2.31}$$

and use the relations

$$L_{\alpha}|k\rangle\langle\ell| = -i\sum_{i}\left[d^{\alpha}_{mk}|m\rangle\langle\ell| - d^{\alpha}_{\ell m}|k\rangle\langle m|\right] \tag{2.32}$$

and

$$(\omega - iL_o)^{-1}|k\rangle\langle\ell| = (\omega-\Lambda_{k\ell})^{-1}(1-\delta_{k\ell})|k\rangle\langle\ell| + \delta_{k\ell}\sum_{m} B_{km}(\omega)|m\rangle\langle m| , \tag{2.33}$$

where

$$B_{km}(\omega) = \sum_{n}\frac{S^{-1}_{nk}S_{mn}}{\omega - i\lambda_n} \tag{2.34}$$

Note that (2.33) follows from (2.15) on putting $f(L_o)=(\omega-iL_o)^{-1}$ and $Q=|i><j|$. For the simple relaxation model (2.5) where the population from each level $|k>$ is assumed to leak out of the system at the rate Γ_{kk}, we have $\lambda_\ell = -\Gamma_{\ell\ell}$ so that

$$B_{km}(\omega) \longrightarrow \delta_{km}(\omega+i\Gamma_{kk})^{-1} \qquad (2.35)$$

In view of this, it is useful to introduce a new quantity

$$C_{km}(\omega) = B_{km}(\omega) - \delta_{km}(\omega + i\Gamma_{kk})^{-1} \qquad (2.36)$$

so that $C_{km} \to 0$ for the relaxation model (2.5). Thus the expression (2.33) can be rewritten in the form

$$(\omega-iL_o)^{-1}|k><\ell| = (\omega-\Lambda_{k\ell})^{-1} + \sum_m C_{km}(\omega)|m><m| \qquad (2.37)$$

Using (2.32) and (2.37), we can write down a very useful relation

$$(\omega-iL_o)^{-1}L_\alpha|k><\ell| = -i\sum_m [d^\alpha_{mk}(\omega-\Lambda_{m\ell})^{-1}|m><\ell| - d^\alpha_{\ell m}(\omega-\Lambda_{km})^{-1}|k><m|$$

$$+ d^\alpha_{\ell k}\left(C_{\ell m}(\omega)-C_{km}(\omega)\right)|m><m|\ ] \qquad (2.38)$$

The repeated use of (2.38) in (2.30) makes the calculation of the general expressions for susceptibilities to any order n a straightforward matter. In subsequent sections, we consider the explicit forms of (2.30) for various values of n.

III. FIRST-ORDER RESPONSE

We use the general structure (2.30) to examine the effect of damping on the linear response function which can be simply written down using (2.38) in (2.30)

$$\chi^{(1)}_{\mu\alpha}(\omega) = N \sum_{k\ell}^{-} d^{\mu}_{\ell k}\, d^{\alpha}_{k\ell} \left[\rho^{(o)}_{kk} - \rho^{(o)}_{\ell\ell}\right] \left[\omega - \omega_{k\ell} + i\Gamma_{k\ell}\right]^{-1} \tag{2.39}$$

The first-order response function has the usual form but the frequency $\omega_{k\ell}$ is replaced by the complex frequency $\omega_{k\ell} - i\Gamma_{k\ell}$. $\chi^{(1)}$ is thus essentially independent of the relaxation model as it is determined solely from the relaxation of off-diagonal elements of the density matrix. Inelastic collisional rates are included in $\Gamma_{k\ell}$. The phenomenogical replacement $\omega_{k\ell} \rightarrow \omega_{k\ell} - i\Gamma_{k\ell}$ is justified here.

IV. SECOND-ORDER RESPONSE

We calculate the explicit form of the second-order response function $\chi^{(2)}$. Here the model of relaxation can make substantial difference in the structure. From (2.30), the second-order response function $\chi^{(2)}$ is

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = -\frac{N}{2}\, \text{sym Tr} \left\{ d^{\mu}(\omega_1 + \omega_2 - iL_o)^{-1} L_{\alpha}(\omega_2 - iL_o)^{-1} L_{\beta}\rho^{(o)} \right\} . \tag{2.40}$$

which on using (2.38) reduces to

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = \frac{iN}{2}\,\mathrm{sym}\sum_{lm}^{-}\left[\rho^{(o)}_{ll}-\rho^{(o)}_{mm}\right] d^{\beta}_{ml}\left(\omega_2-\Lambda_{ml}\right)^{-1}$$

$$\times\ \mathrm{Tr}\left\{d^{\mu}\left(\omega_1+\omega_2-iL_o\right)^{-1} L_{\alpha}|m><l|\right\} \quad . \qquad (2.41)$$

On using (2.38) once again in Eq.(2.41), we obtain

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = \frac{N}{2}\,\mathrm{sym}\sum_{lmJ}^{-}\left[\rho^{(o)}_{ll}-\rho^{(o)}_{mm}\right] d^{\beta}_{ml}\left(\omega_2-\Lambda_{ml}\right)^{-1}$$

$$\times\ \left[d^{\alpha}_{Jm}\, d^{\mu}_{lJ}\left(\omega_1+\omega_2-\Lambda_{Jl}\right)^{-1} - d^{\alpha}_{lJ}d^{\mu}_{Jm}\left(\omega_1+\omega_2-\Lambda_{mJ}\right)^{-1}\right.$$

$$\left. +\ d^{\alpha}_{lm}d^{\mu}_{JJ}\left[\,C_{lJ}(\omega_1+\omega_2) - C_{mJ}(\omega_1+\omega_2)\right]\right] \quad . \qquad (2.42)$$

We now give the complete symmetrized form of $\chi^{(2)}$. We adopt the notation[5] of Bloembergen et al. for writing the product of dipole matrix elements: $\mu\alpha\beta$ will stand for $d^{\mu}_{lk}d^{\alpha}_{kJ}d^{\beta}_{Jl}$. The symmetrized form is

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = \frac{N}{2}\sum_{lJk}^{-}\rho^{(o)}_{ll}\left\{ d_{lk}d_{kJ}d_{Jl}\left[\frac{\mu\alpha\beta}{(\omega_p-\Lambda_{kl})(\omega_2-\Lambda_{Jl})}\right.\right.$$

$$+\ \frac{\beta\alpha\mu}{(\omega_p-\Lambda_{lJ})(\omega_2-\Lambda_{lk})} - \frac{\alpha\mu\beta}{\omega_p-\Lambda_{Jk}}\left(\frac{1}{\omega_1-\Lambda_{lk}}+\frac{1}{\omega_2-\Lambda_{Jl}}\right)\left.\right]$$

$$+\ d^{\alpha}_{lk}d^{\beta}_{kl}d^{\mu}_{JJ}\left(\frac{1}{\omega_1-\Lambda_{lk}}+\frac{1}{\omega_2-\Lambda_{kl}}\right)\left(C_{lJ}(\omega_p) - C_{kJ}(\omega_p)\right)$$

$$\left. +\ \left(\begin{matrix}\alpha\\ \omega_1\end{matrix}\right) \leftrightarrow \left(\begin{matrix}\beta\\ \omega_2\end{matrix}\right)\right\} \quad , \quad \omega_p = \omega_1+\omega_2 \quad . \qquad (2.43)$$

Note that () ↔ (), indicates a permutation, i.e., an interchanging of the specified indices. The expression (2.43) includes cont-

ributions 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.[5] In the special case of a two-level system, [see Fig.1] the eigenvalues λ can be calculated explicitly and we obtain the following result for $\chi^{(2)}$.

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = \frac{N}{2}\left(\rho^{(o)}_{11} - \rho^{(o)}_{22}\right)\left\{\left(d^{\alpha}_{22}-d^{\alpha}_{11}\right)\left[\frac{d^{\beta}_{12}\,d^{\mu}_{21}}{(\omega_p-\Lambda_{12})(\omega_2-\Lambda_{12})}\right.\right.$$

$$\left. + \frac{d^{\mu}_{12}\,d^{\beta}_{21}}{(\omega_p-\Lambda_{21})(\omega_2-\Lambda_{21})}\right] - \frac{(d^{\mu}_{22}-d^{\mu}_{11})d^{\alpha}_{12}\,d^{\beta}_{21}}{i(\gamma_{12}+\gamma_{21})+\omega_p}\left(\frac{1}{\omega_1-\Lambda_{12}}+\frac{1}{\omega_2-\Lambda_{21}}\right)$$

$$\left. + \begin{pmatrix}\alpha\\ \omega_1\end{pmatrix} \leftrightarrow \begin{pmatrix}\beta\\ \omega_2\end{pmatrix}\right\}, \qquad (2.44)$$

which is obviously non-zero if $d_{11} \neq d_{22} \neq 0$. In addition to various resonances at $\omega_{12}=\omega_1,\omega_2,\omega_p$, 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 $\omega_1+\omega_2=0$. The general expression for $\chi^{(2)}$ (2.43) 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 too is 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 Section II, the population N_i of the i^{th} level in steady state will be

$$N_i = \sum_{\alpha\beta} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \, e^{-i(\omega_1+\omega_2)t} \, \mathcal{M}^{(2)}_{i\alpha\beta}(\omega_1,\omega_2) E_\alpha(\omega_1) E_\beta(\omega_2) \quad , \tag{2.45}$$

where $\mathcal{M}^{(2)}_{i\alpha\beta}(\omega_1,\omega_2)$ can be obtained from (2.43) if we replace d^μ 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 modulation spectroscopy. For example, the modulated fluorescence at Ω will be determined by

$$\mathcal{M}^{(2)}_{i\alpha\beta}(\omega + \Omega, -\omega) \quad , \quad \mathcal{M}^{(2)}_{i\alpha\beta}(-(\omega - \Omega), \omega) \quad .$$

From (2.43) it is clear that the inelastic collision terms [the matrix elements of $C(\omega_p)$-$C(\omega_1+\omega_2)$] resonate at Ω=0 with a width that is determined by inelastic collisions. Other terms resonate when $\omega \pm \Omega$ equals the atomic frequencies $\omega_{k\ell}$. In particular for the case of a two-level atom, Eq.(2.44) shows that the inelastic collision term $[\omega_p + i(\gamma_{12}+\gamma_{21})]$ resonates when Ω=0 and such a resonance has a width $\gamma_{12}+\gamma_{21}$. Thus for the off-resonant case, the peak at Ω=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 Ω=0 will dominate as it is unaffec-

ted by Doppler broadening whereas other resonances $\omega \pm \Omega = \omega_{k\ell}$ 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[39] that showed that T_1 can be determined for a Doppler-broadened two-level system by doing modulation spectroscopy.

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

In this section we consider the general structure of the 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 (2.30) by the repeated application of (2.38). The complete symmetrized expression for $\chi^{(3)}$ is given by

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = \frac{N}{6}\left[B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) \right] \qquad (2.46)$$

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

$$B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = \sum_{lnkJ} \rho^{(o)}_{ll}\, d_{ln} d_{nk} d_{kJ} d_{Jl}$$

$$\times \left\{ \left[- \frac{\mu\ \alpha\beta\gamma}{(\omega_p-\Lambda_{ni})(\omega_2+\omega_3-\Lambda_{ki})(\omega_3-\Lambda_{ji})} + \frac{\alpha\beta\gamma\mu}{(\omega_p-\Lambda_{ij})(\omega_1+\omega_2-\Lambda_{ik})(\omega_1-\Lambda_{in})} \right.\right.$$

$$+ \frac{\alpha\mu\beta\gamma}{\omega_p-\Lambda_{kn}} \left[\frac{1}{(\omega_2+\omega_3-\Lambda_{ki})(\omega_3-\Lambda_{ji})} + \frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_3-\Lambda_{ji})} \right.$$

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

$$\left.\left. + \frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_3-\Lambda_{ji})} + \frac{1}{(\omega_1+\omega_2-\Lambda_{ik})(\omega_1-\Lambda_{in})} \right] \right]$$

$$+ \text{ terms obtained by using permutations}$$

$$\begin{bmatrix} \alpha & \beta & \gamma \\ \omega_1 & \omega_2 & \omega_3 \end{bmatrix} \longrightarrow \begin{bmatrix} \alpha & \gamma & \beta \\ \omega_1 & \omega_3 & \omega_2 \end{bmatrix}, \begin{bmatrix} \beta & \alpha & \gamma \\ \omega_2 & \omega_1 & \omega_3 \end{bmatrix}, \begin{bmatrix} \beta & \gamma & \alpha \\ \omega_2 & \omega_3 & \omega_1 \end{bmatrix}$$

$$\left. \begin{bmatrix} \gamma & \alpha & \beta \\ \omega_3 & \omega_1 & \omega_2 \end{bmatrix}, \begin{bmatrix} \gamma & \beta & \alpha \\ \omega_3 & \omega_2 & \omega_1 \end{bmatrix} \right\} . \qquad (2.47)$$

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

$$C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = \sum_{inkj}^{-} \rho^{(o)}_{ii} d_{kn} d_{nk} d_{ij} d_{ji} \left\{ \frac{A(\omega_2+\omega_3)}{\omega_p-\Lambda_{nk}} \right.$$

$$\times \left[\mu\alpha\beta\gamma \left(\frac{1}{\omega_2-\Lambda_{ij}} + \frac{1}{\omega_3-\Lambda_{ji}} \right) + \begin{pmatrix} \beta \\ \omega_2 \end{pmatrix} \leftrightarrow \begin{pmatrix} \gamma \\ \omega_3 \end{pmatrix} \right] + \begin{pmatrix} \alpha \\ \omega_1 \end{pmatrix} \leftrightarrow \begin{pmatrix} \beta \\ \omega_2 \end{pmatrix}$$

$$\left. + \begin{pmatrix} \alpha \\ \omega_1 \end{pmatrix} \leftrightarrow \begin{pmatrix} \gamma \\ \omega_3 \end{pmatrix} \right\} ,$$

$$A(\omega) = C_{jk}(\omega) + C_{in}(\omega) - C_{jn}(\omega) - C_{ik}(\omega) \quad , \qquad (2.48)$$

$$D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = \sum^{-}_{lmnk} \rho^{(o)}_{mm} d_{mn} d_{nk} d_{km} d_{ll}$$

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

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

+ five permutations

$$\begin{pmatrix} \alpha & \beta & \gamma \\ \omega_1 & \omega_2 & \omega_3 \end{pmatrix} \rightarrow \begin{pmatrix} \alpha & \gamma & \beta \\ \omega_1 & \omega_3 & \omega_2 \end{pmatrix}, \begin{pmatrix} \beta & \alpha & \gamma \\ \omega_2 & \omega_1 & \omega_3 \end{pmatrix}, \begin{pmatrix} \beta & \gamma & \alpha \\ \omega_2 & \omega_3 & \omega_1 \end{pmatrix},$$

$$\left. \begin{pmatrix} \gamma & \alpha & \beta \\ \omega_3 & \omega_1 & \omega_2 \end{pmatrix}, \begin{pmatrix} \gamma & \beta & \alpha \\ \omega_3 & \omega_2 & \omega_1 \end{pmatrix} \right\} \quad , \qquad (2.49)$$

This is the most general form of $\chi^{(3)}$ for a system undergoing relaxation described by 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.[5] 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 by the inelastic collisions; moreover, such Rayleigh-like terms also have the possibility of two intermediate states (e.g., $|n\rangle$ and $|k\rangle$ in Eq.(2.48), not connected to the initially populated level $|i\rangle$ by any dipole transition) resonating with one of the applied frequencies. Terms like

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

in $B^{(3)}$ lead to the pressure-induced extra resonances[5,37,40] as discussed by Bloembergen et al. Note that such additional resonances occur in $D^{(3)}$ too (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 (2.46).

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

In special cases where the transitions among only few levels are important, the 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 the two levels are connected by a two-photon

transition (cf. Ref.41). Calculations using (2.46) show that the relevant susceptibility is

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega,\ \omega,\ -\omega) = -\frac{N}{3!}\frac{(\rho^{(o)}_{11}-\rho^{(o)}_{22})(d^{\alpha}_{11}-d^{\alpha}_{22})d^{\beta}_{12}}{(2\omega-\Lambda_{12})(\omega-\Lambda_{12})}\left[\frac{(d^{\gamma}_{11}-d^{\gamma}_{22})d^{\mu}_{21}}{\omega-\Lambda_{12}}\right.$$

$$\left. - \frac{(d^{\mu}_{11}-d^{\mu}_{22})d^{\gamma}_{21}}{\omega+i(\gamma_{12}+\gamma_{21})}\right], \quad \rho^{(o)}_{11}\gamma_{21} = \gamma_{12}\rho^{(o)}_{22} . \qquad (2.50)$$

Note that in writing expression (2.50), we have thrown away the non-rotating terms. Hence the expression in (2.50) does not have the symmetry with respect to the permutations of the indices $(\alpha,\omega),(\beta,\omega),(\gamma,-\omega)$ since the non-rotating terms corresponds to contributions from some of the permutations. The susceptibility in Eq.(2.50) appears in the coefficients in propagation equations for the probe and conjugate waves. Such susceptibilities will also be needed for the description of the basic modes of the two-photon media.[42,43]

B. Pump-probe experiments in ruby

We consider another example where inelastic collisions are important. Consider optical transitions in ruby,[19] which is essentially a three-level system [see Fig.2]. Expression (2.46) 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 presence of a pump beam and four-wave mixing.

$$\chi^{(3)}(\omega_1, -\omega_1, \omega_2) = \frac{2N}{3!} \frac{(\rho_{11}^{(o)} - \rho_{22}^{(o)})|d_{12}|^4}{\omega_2 - \Lambda_{12}} \left[C(o) \left(\frac{1}{\omega_1 - \Lambda_{12}} + \frac{1}{-\omega_1 - \Lambda_{21}} \right) \right.$$

$$\left. + C(\omega_2 - \omega_1) \left(\frac{1}{\omega_2 - \Lambda_{12}} + \frac{1}{-\omega_1 - \Lambda_{21}} \right) \right] , \qquad (2.51)$$

$$\chi^{(3)}(\omega_1, \omega_1, -\omega_2) = \frac{2N}{3!} \frac{(\rho_{11}^{(o)} - \rho_{22}^{(o)})|d_{12}|^4 C(\omega_1 - \omega_2)}{2\omega_1 - \omega_2 - \Lambda_{12}} \left(\frac{1}{\omega_1 - \Lambda_{12}} + \frac{1}{-\omega_2 - \Lambda_{21}} \right) \qquad (2.52)$$

Note that we have assumed all fields to be polarized in the same direction and hence dropped the tensor indices in the expressions (2.51) and (2.52). Further note that the expressions in (2.51), (2.52) do not exhibit the symmetry with respect to permutations of the frequencies since in writing these expressions, we have thrown away the non-rotating terms. The non-rotating terms correspond to contributions from some of the permutations. In the expressions (2.51) and (2.52) the phase-changing collisions enter through Λ_{12} and the inelastic collisions enter through $C(\omega)$,

$$C(\omega) = \frac{i(\gamma_{31} + 2\gamma_{23}) + 2\omega}{(i\lambda_1 - \omega)(i\lambda_2 - \omega)} \qquad (2.53)$$

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

$$\lambda^2 + (\gamma_{12} + \gamma_{21} + \gamma_{31} + \gamma_{23})\lambda + (\gamma_{23}\gamma_{12} + \gamma_{23}\gamma_{31} + \gamma_{12}\gamma_{31} + \gamma_{23}\gamma_{21}) = 0 , \qquad (2.54)$$

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

$$\rho_{11}^{(o)} - \rho_{22}^{(o)} = \gamma_{23}(\gamma_{12}-\gamma_{21}-\gamma_{31})/[\gamma_{12}\gamma_{31}+\gamma_{23}(\gamma_{12}+\gamma_{21}+\gamma_{31})] \tag{2.55}$$

The transfer of population from 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

$$C(\omega) \longrightarrow \frac{2}{\omega+i(\gamma_{21}+\gamma_{31})} + \frac{i\gamma_{31}}{[\omega+i(\gamma_{21}+\gamma_{31})](\omega+i\gamma_{23})} \tag{2.56}$$

In this limit, the four-wave mixing susceptibility for ruby [Eq. (2.52)] can be written in the form

$$\chi^{(3)}(\omega_1, \omega_1, -\omega_2) = -\frac{2N}{3!} \frac{(\rho_{11}^{(o)}-\rho_{22}^{(o)})|d_{12}|^4}{(2\omega_1-\omega_2-\Lambda_{12})(\omega_1-\Lambda_{12})(-\omega_2-\Lambda_{21})}$$

$$\times \frac{\Lambda_{12}+\Lambda_{21}-\omega_1+\omega_2}{\omega_1-\omega_2+i(\gamma_{21}+\gamma_{31})} \left[2 + \frac{i\gamma_{31}}{\omega_1-\omega_2+i\gamma_{23}} \right] \tag{2.57}$$

In the absence of phase-changing collisions, the term $[\omega_1-\omega_2+i(\gamma_{21}+\gamma_{31})]^{-1}$ cancels, since $\Lambda_{12}+\Lambda_{21} = -i(\gamma_{21}+\gamma_{31})-2i\Gamma_{12}^{ph}$. Hence in the two-level limit, i.e., when $\gamma_{31}=0$, a resonance at $\omega_2=\omega_1$ is present in the four-wave mixing susceptibility only if phase-changing collisions are present. Systems such as ruby can be regarded as open two-level systems (in contrast to the closed two-level systems with $\gamma_{31}=0$) in the sense that the two levels $|1\rangle$ and $|2\rangle$ are constantly exchanging energy with a third level $|3\rangle$ outside the system. Hence in such a system, a resonance at $\omega_2=\omega_1$ with width γ_{23} is always present. In the case of ruby, the various

decay rates[44] are: $\gamma_{31}\sim 2 \times 10^7$/sec, $\gamma_{21}=3 \times 10^5$/sec, $\gamma_{23}=10^3/3$/sec. Thus since γ_{23} is much smaller than the other decay rates, an extremely narrow resonance at $\omega_2=\omega_1$ should be seen in the four-wave mixing signals in ruby. In recent years, such ultranarrow resonances have been observed in open two-level systems that are similar to ruby.[45]

In conclusion, we have developed a Liouville operator formulation of nonlinear response theory of a quantum mechanical system undergoing arbitrary relaxation and interacting with external fields. Explicit expressions for the second and third-order susceptibilities of a system undergoing phase-changing and inelastic collisions are obtained. The inelastic collisions give rise to additional terms in the nonlinear susceptibilities. These terms resonate when some combinations of the applied field frequencies vanish. The general structure suggests how the additional resonances can be used to determine the inelastic rates in a Doppler-broadened medium. In particular, it is evident from the expression for the second-order susceptibility that the fluorescence signal under excitation by a modulated field exhibits a resonance at zero modulation frequency the width of which is determined by the inelastic collisions in the system. Our result for the third-order response is useful in determining the coefficients in the propagation equations in the case of phase conjugation via four-wave mixing. It is also useful for the discussion of the pump-probe experiments in systems such as ruby where the inelastic collisions are important.

CHAPTER III

DIAGRAMMATIC CALCULATION OF THE INELASTIC CONTRIBUTIONS TO THE NONLINEAR SUSCEPTIBILITIES

Diagrammatic methods of calculation of nonlinear optical response have been quite popular in the literature.[46-51] One distinct advantage of such methods is that since each term in the expression for the nonlinear susceptibility is represented by a diagram, it is possible to interpret the contribution from each term to a particular process in physical terms. Yee et al[45] calculated the third-order susceptibility taking into account the effect of damping (phase-changing collisions and the decay of level populations out of the system) systematically by using double-sided Feynman diagrams. Such diagrams have been extensively used to analyse various nonlinear optical processes, both under cw and pulsed excitations. Prior[27] wrote down the diagrams corresponding to all the forty eight terms occuring in the third-order susceptibility derived by Bloembergen et al.[5] Recently, Trebino et al[52] have studied the higher order dephasing-induced effects using the diagrammatic approach.

In Chapter II, we calculated the nonlinear response taking into account a more general relaxation model that included phase-changing collisions as well as the inelastic collisions. We also gave explicit expressions for the second and third-order nonlinear

susceptibilities and showed that the inelastic collisions give rise to additional resonant contributions. In this chapter, we generalize the existing diagrammatic method and use it to calculate the nonlinear susceptibilities for systems exhibiting a more general relaxation behaviour. In Section II, we show the formal equivalence between the diagrammatic method of calculation of the nonlinear susceptibilities and the method based on the solution of the Liouville equation for the density operator (which we refer to as the algebraic method). We show that the basic components involved in the diagrammatic method can in fact be traced in the algebraic method. In Section III, we describe the diagrammatic method and give the prescription on how a particular diagram can be translated into a term in the nonlinear susceptibility. In Section IV, we show how the effects of inelastic collisions can be incorporated into the diagrams and illustrate how the prescription given in Section III can be used to translate such diagrams into the corresponding inelastic terms. In Section V and VI, we present the diagrammatic calculation respectively of the second-order susceptibility and the inelastic contributions to the third-order susceptibility. Finally, we illustrate the general diagrammatic method by calculating the four-wave mixing susceptibility of ruby where the inelastic contributions are important.

II. ALGEBRAIC BASIS OF THE DIAGRAMMATIC METHOD

By solving the density matrix equations of motion for a system undergoing arbitrary relaxation and interacting with

external fields, we have obtained in Chapter II, an expression for the n^{th} order nonlinear susceptibility

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}) = \frac{N(-i)^n}{n!}\,\mathrm{sym\ Tr}\left\{ d^{\mu} D\Big(\sum_{i=1}^{n}\omega_i\Big) \times L_{\alpha_1} D\Big(\sum_{i=2}^{n}\omega_i\Big) L_{\alpha_2} \ldots D(\omega_n) L_{\alpha_n} \rho^{(o)} \right\}, \quad L_{\alpha} \equiv -i\,[d^{\alpha}, \ ] \tag{3.1}$$

where we have defined

$$D(\omega) = (\omega - iL_o)^{-1} \tag{3.2}$$

Here L_o contains the effects of relaxation [Eq.(2.3)] and L_α contains the effect of external fields. As emphasized earlier, the usual calculation of $\chi^{(n)}$ for a multilevel system consists of writing

$$\rho^{(o)} = \sum_{i} \rho^{(o)}_{ii}\, |i\rangle\langle i| \tag{3.3}$$

and then evaluating successively the action of the various L_α's and $D(\omega)$'s occuring in the expression (3.1). Consider the action of the (Liouville) operator L_α, on a vector (in the Liouville space) $|i\rangle\langle j|$. We have

$$L_{\alpha}|i\rangle\langle j| = -i \sum_{k} \left[d^{\alpha}_{ki} |k\rangle\langle j| + (-d^{\alpha}_{jk}) |i\rangle\langle k| \right] . \tag{3.4}$$

Thus, it is clear from Eq.(3.4) that L_α transforms both the |ket> and <bra| parts of the vector $|i\rangle\langle j|$, separately, as a result of

field-induced transitions from $|i\rangle$ to $|k\rangle$ and from $|k\rangle$ to $|j\rangle$ respectively. Similarly, consider the action of $D(\omega)$ on a vector $|i\rangle\langle j|$. We have

$$D(\omega)|i\rangle\langle j| = \sum_{k\ell} D_{ijk\ell}(\omega)\,|k\rangle\langle\ell| \quad . \tag{3.5}$$

Here, again we see that $D(\omega)$, which is related to the relaxation operator L_o [Eq.(3.2)], in general transforms both the |ket> and <bra| parts of the vector $|i\rangle\langle j|$. Note that for the relaxation model which includes phase-changing and inelastic collisions, Eq. (3.5) has a simple structure

$$D(\omega)|i\rangle\langle j| = (\omega-\Lambda_{ij})^{-1}(1-\delta_{ij})|i\rangle\langle j| + \delta_{ij}\sum_k B_{ik}(\omega)|k\rangle\langle k| \quad , \tag{3.6}$$

where $B_{ik}(\omega)$ is as defined by Eq.(2.34). Thus we see that for $i\neq j$, $D(\omega)$ does not transform the vector $|i\rangle\langle j|$, but for $i=j$, $D(\omega)$ transforms the vector $|i\rangle\langle i|$ into another vector $|k\rangle\langle k|$. Equation (3.6) can be rewritten in the form

$$D(\omega)\,|i\rangle\langle j| = (\omega-\Lambda_{ij})^{-1}|i\rangle\langle j| + \delta_{ij}\sum_k C_{ik}(\omega)|k\rangle\langle k|$$

$$C_{ik}(\omega) = B_{ik}(\omega) - \delta_{ik}(\omega + i\Gamma_{ii})^{-1} \tag{3.7}$$

For the simple relaxation model which does not include state-changing collisions, $C(\omega) \to 0$. In such a case the action of $D(\omega)$ on $|i\rangle\langle j|$ is merely to multiply the same by a factor $(\omega-\Lambda_{ij})^{-1}$

However, for the case of arbitrary relaxation, $D(\omega)$ does transform $|i\rangle\langle j|$ into something else. The diagrammatic method of calculation of $\chi^{(n)}$ basically involves keeping track of the evolution of the |ket> and <bra| parts of the initial vector $|i\rangle\langle i|$, and assigning appropriate propagation factors at each step. Before proceeding further, it is important to understand the physical meaning of the inelastic term $B_{ij}(\omega)$. In the absence of external fields, the level populations at two different times obey the relation

$$\rho_{ii}^{(o)}(t+\tau) = \sum_k \tilde{R}_{ik}(\tau)\, \rho_{kk}^{(o)}(t) \quad , \quad \tilde{R}(\tau) = e^{R\tau} \quad , \quad \tau > 0 \quad , \qquad (3.8)$$

where R is the population relaxation matrix, $R_{ij}=\gamma_{ij}(i\neq j)$, $R_{ii}=-\sum_k \gamma_{ki}$, and the γ_{ij} are rates of inelastic collisions. It is clear from (3.8) that $\tilde{R}_{ik}(\tau)$ is the probability that the atom is in level |i> at time $t+\tau$, given that it was in level |k> at an earlier time t. Thus, $\tilde{R}_{ik}(\tau)$ is non-zero only if there is a relaxation-induced transition from |k> to |i> either directly, or via some other level |n>. The following relation holds between $\tilde{R}(\tau)$ and $B(\omega)$.

$$B_{ij}(\omega) = -i \int_0^\infty d\tau\, e^{i\omega\tau}\, \tilde{R}_{ji}(\tau) \quad . \qquad (3.9)$$

Thus, it follows from Eq.(3.9) that $B_{ij}(\omega)$ is non-zero only if there is a relaxation-induced transition from |i> to |j> either directly, or via some other level |n>.

III. DESCRIPTION OF THE DIAGRAMMATIC METHOD

We describe the main features of the diagrammatic method by considering the example of a third-order process. One possible path of evolution of the initial vector $|m\rangle\langle m|$ can be symbolically written as

$$|m\rangle\langle m| \longrightarrow |\ell\rangle\langle m| \longrightarrow |n\rangle\langle m| \longrightarrow |n\rangle\langle r| \qquad (3.10)$$

Assume that the fields ω_c, ω_b and ω_a act on the system in that time order, with ω_a acting at the latest time. To begin with, consider the case when there are no inelastic collisions. We represent the path of evolution in (3.10) by the following double-sided diagram.

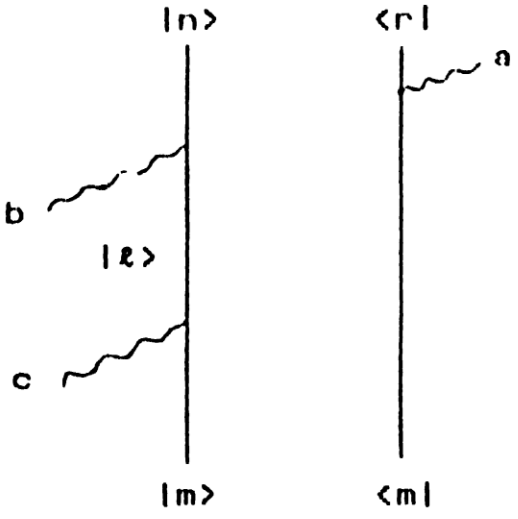


Fig.(a)

Various topologies of diagrams exist in the literature. However, we use diagrams that are very similar to those of Prior.[27] Thus one plots two parallel lines with time advancing upward. A photon absorbed (or emitted) is symbolized by a wavy arrow pointing upward (or downward) when tracing it from left to right. There are basically $2^3=8$ ways of placing three field interactions on the

two sides. Thus the third-order process involves eight basic diagrams. If one considers all possible time orders in which ω_c, ω_b and ω_a act on the system, then one has a total of $8\times3!=48$ diagrams. We will now give the prescription on how to translate the diagram in Fig.(a) into a term in the expression for the third-order suceptibility. The same prescription applies to all other diagrams. The term corresponding to the diagram in Fig.(a) includes the following factors:

(1) Initial density matrix element $\rho^{(o)}_{mm}$.

(2b) A product of four dipole matrix elements

$$(-d^{\alpha}_{mr})d^{\mu}_{rn}d^{\beta}_{n\ell}d^{\gamma}_{\ell m}$$

where α, β, γ, μ refer to the cartesian coordinates of the polarization of the applied fields ω_α, ω_b, ω_c and the generated field $\omega_p(=\omega_a+\omega_b+\omega_c)$ respectively. In writing these matrix elements, we have used Eq.(3.4). Thus the evolution of the ket vector $|i\rangle$ into $|j\rangle$ leads to d_{ji} whereas the evolution of the bra vector $\langle i|$ into $\langle j|$ leads to $-d_{ij}$. The polarization index of the dipole matrix element $d_{\ell m}$ is γ since the field ω_c is acting between the states $|m\rangle$ and $|\ell\rangle$ and so on. Note that the dipole matrix element with index μ is d^{μ}_{rn} since the terminal vector in the diagram is $|n\rangle\langle r|$.

(3b) A product of three propagators. In writing down these, we use Eq.(3.7). Advance in time until after you have crossed an interaction vertex. If the vector at that point is $|\alpha\rangle\langle\beta|$, then the propagator is given by $(\omega-\Lambda_{\alpha\beta})^{-1}$, where ω denotes by the sum of all photon frequencies pointing upward minus the sum of all

photon frequencies pointing downward, below that vertex. For the diagram in Fig.(a), the vector at the point after the first photon ω_c has been absorbed is $|\ell\rangle\langle m|$. Hence the first propagator is given by $(\omega_c-\Lambda_{\ell m})^{-1}$. The vector after the first two fields ω_c and ω_b have been absorbed is $|n\rangle\langle m|$. Hence the second propagator is $(\omega_b+\omega_c-\Lambda_{nm})^{-1}$. Similarly, the vector after all the three photons ω_c, ω_b and ω_a have been absorbed is $|n\rangle\langle r|$. Hence the last propagator is $(\omega_a+\omega_b+\omega_c-\Lambda_{nr})^{-1}=(\omega_p-\Lambda_{nr})^{-1}$.

(4) A factor of $(-1)^3$.

Thus the term corresponding to the diagram in Fig.(a) is given by the product of the factors in (1)-(4) above, namely

$$T_B = (-1)^3 \frac{\rho^{(o)}_{mm}(-d^{\alpha}_{mr})d^{\mu}_{rn}d^{\beta}_{n\ell}d^{\gamma}_{\ell m}}{(\omega_p-\Lambda_{nr})(\omega_b+\omega_c-\Lambda_{nm})(\omega_c-\Lambda_{\ell m})} \qquad (3.11)$$

IV. DIAGRAMS FOR THE INELASTIC TERMS

In the analysis in Section III, we assumed a relaxation model that did not include inelastic collisions. Hence to the extent that double-sided diagrams are used, the structure of the diagrams is the same as in the absence of relaxation (as also the structure of the corresponding terms, except that ω_{ij} is replaced by $\Lambda_{ij}=\omega_{ij}-i\Gamma_{ij}$). However, when inelastic collisions are present, there is a significant modification in the structure of the diagrams as well as the corresponding terms. We now illustrate the

method for writing down the diagrams which yield the terms that arise due to the inelastic collisions. In the symbolic expression (3.10) of the path of evolution of the initial vector $|m\rangle\langle m|$, consider the possibility of the state $|n\rangle$ being the same as $|m\rangle$. In such a case the path of evolution will be

$$|m\rangle\langle m| \longrightarrow |\ell\rangle\langle m| \longrightarrow |m\rangle\langle m| \Longrightarrow |j\rangle\langle j| \longrightarrow |j\rangle\langle r| \ . \tag{3.12}$$

The double arrow in (3.12) indicates that a relaxation-induced transition has taken place from level $|m\rangle$ to $|j\rangle$. The path in (3.12) can be represented by the following double-sided diagram.

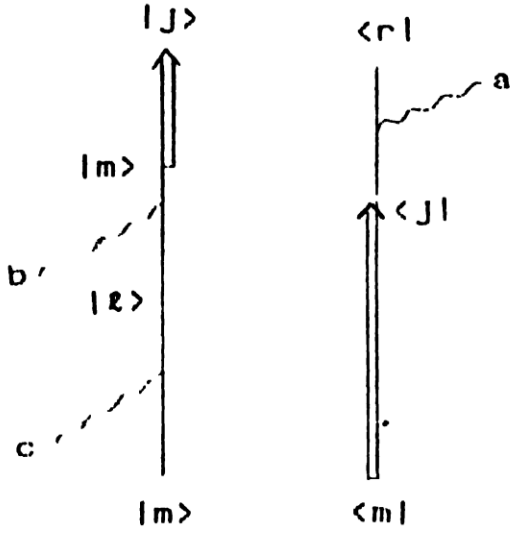


Fig.(b)

Note that the double arrows in the diagram in Fig.(b) signify the fact that a relaxation-induced transition from $|m\rangle$ to $|j\rangle$ has taken place, after the first two photons ω_c and ω_b have been absorbed. We now give the prescription on how to translate the diagram in Fig.(b) into the corresponding term in the expression for $\chi^{(3)}$. The term will consist of the following factors:

(1) Initial density matrix element $\rho^{(o)}_{mm}$.

(2c) A product of four dipole matrix elements

$$(-d^{\alpha}_{jr})\ d^{\mu}_{rj}\ d^{\beta}_{m\ell}\ d^{\gamma}_{\ell m}$$

where α, β, γ, μ refer to the cartesian components of the polarizations of the applied fields ω_a, ω_b, ω_c and the generated field $\omega_p(=\omega_a+\omega_b+\omega_c)$ respectively. The rule for writing down these dipole matrix elements is the same as in (2b). Thus on the |ket> side we have $d^{\gamma}_{\ell m}$ and $d^{\beta}_{m\ell}$, while on the <bra| side we have $-d^{\alpha}_{jr}$. Since the terminal vector is $|j><r|$, the corresponding dipole matrix element is d^{μ}_{rj}.

(3c) A product of three propagators: In writing down these, we again make use of Eq.(3.7). Advance in time until after you have crossed an interaction vertex. If the vector at the point is $|\alpha><\beta|$ $(\alpha\neq\beta)$, then the propagator is given by $(\omega-\Lambda_{\alpha\beta})^{-1}$, where ω denotes the sum of all photon frequencies pointing upward minus the sum of all photon frequencies pointing downward, below the vertex. However, if the vector at the point is $|\alpha><\alpha|$, then as a result of a relaxation-induced transition, $|\alpha><\alpha|$ evolves into some $|\beta><\beta|$, and hence the propagator is given by $C_{\alpha\beta}(\omega)$ where ω has the meaning as above and $C_{\alpha\beta}(\omega)$ is as defined in Eq.(3.7). Note that in the diagram in Fig.(b), the relaxation-induced transition occurs after the first two photons ω_c and ω_b have been absorbed. Hence the inelastic propagator is given by $C_{mj}(\omega_b+\omega_c)$ We have already shown [Eqs.(3.8),(3.9)] that $B_{\alpha\beta}(\omega)$ and hence, $C_{\alpha\beta}(\omega)$ is related to the possibility of a relaxation-induced

give the prescription for translating the diagram in Fig.(c) into a term in the expression for $\chi^{(3)}$. Again, the term will consist of the following four factors:

(1) Initial density matrix element $\rho^{(o)}_{mm}$.

(2d) A product of four dipole matrix elements

$$d^{\mu}_{jJ}(-d^{\alpha}_{mn})\, d^{\beta}_{n\ell} d^{\gamma}_{\ell m} \quad .$$

The rule for writing down these matrix elements is the same as in (2b) and (2c).

(3d) A product of three propagators: The rule for writing down the propagators is same as in (3c), that as you advance in time, if the vector at a point just after an interaction vertex is $|\alpha\rangle\langle\beta|$ $(\alpha\neq\beta)$ then the propagator is $(\omega-\Lambda_{\alpha\beta})^{-1}$ while if the vector is $|\alpha\rangle\langle\alpha|$ followed by a relaxation-induced transition to $|\beta\rangle\langle\beta|$, then the propagator is $C_{\alpha\beta}(\omega)$, where ω, as in (3b) and (3c) is given by the sum of all photon frequencies pointing upward minus the sum of all photon frequencies pointing downward, below that vertex. Note that unlike in the diagram in Fig.(b), the relaxation-induced transition in the diagram in Fig.(c) occurs after all the photons ω_c, ω_b and ω_a have been abosrbed. Hence the inelastic propagator here is given by $C_{nJ}(\omega_a+\omega_b+\omega_c) = C_{nJ}(\omega_p)$. The first and the second propagators have the usual structure, and these are respectively given by $(\omega_c-\Lambda_{\ell m})^{-1}$ and $(\omega_b+\omega_c-\Lambda_{nm})^{-1}$.

(4) A factor of $(-1)^3$.

give the prescription for translating the diagram in Fig.(c) into a term in the expression for $\chi^{(3)}$ Again, the term will consist of the following four factors:

(1) Initial density matrix element $\rho^{(o)}_{mm}$

(2d) A product of four dipole matrix elements

$$d^{\mu}_{jj}(-d^{\alpha}_{mn})\, d^{\beta}_{n\ell} d^{\gamma}_{\ell m}$$

The rule for writing down these matrix elements is the same as in (2b) and (2c).

(3d) A product of three propagators: The rule for writing down the propagators is same as in (3c), that as you advance in time, if the vector at a point just after an interaction vertex is $|\alpha\rangle\langle\beta|$ $(\alpha\neq\beta)$ then the propagator is $(\omega-\Lambda_{\alpha\beta})^{-1}$ while if the vector is $|\alpha\rangle\langle\alpha|$ followed by a relaxation-induced transition to $|\beta\rangle\langle\beta|$, then the propagator is $C_{\alpha\beta}(\omega)$, where ω, as in (3b) and (3c) is given by the sum of all photon frequencies pointing upward minus the sum of all photon frequencies pointing downward, below that vertex. Note that unlike in the diagram in Fig.(b), the relaxation-induced transition in the diagram in Fig.(c) occurs after all the photons ω_c, ω_b and ω_a have been abosrbed. Hence the inelastic propagator here is given by $C_{nj}(\omega_a+\omega_b+\omega_c) = C_{nj}(\omega_p)$. The first and the second propagators have the usual structure, and these are respectively given by $(\omega_c-\Lambda_{\ell m})^{-1}$ and $(\omega_b+\omega_c-\Lambda_{nm})^{-1}$.

(4) A factor of $(-1)^3$.

Thus the term corresponding to the diagram in Fig.(c) will be given by

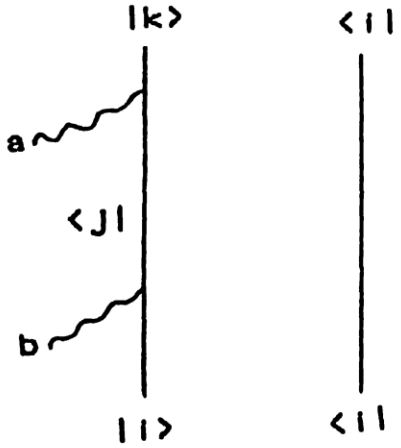
$$T_D = (-1)^3 \frac{\rho^{(o)}_{mm} d^{\mu}_{JJ} (-d^{\alpha}_{mn}) d^{\beta}_{n\ell} d^{\gamma}_{\ell m}}{(\omega_b+\omega_c-\Lambda_{nm})(\omega_c-\Lambda_{\ell m})} C_{nJ}(\omega_p) \qquad (3.15)$$

Note that the terms T_B, T_C and T_D in (3.11), (3.13) and (3.15) occur respectively in $B^{(3)}$ [Eq.(2.47)], $C^{(3)}$ [Eq., (2.48)] and $D^{(3)}$ [Eq.(2.49)] in the general expression for $\chi^{(3)}$ given in Chapter II. Thus we see that corresponding to each one of the usual diagrams [as in Fig.(a)], there are in general two additional diagrams [as in Figs.(b) and (c)] that arise due to the presence of inelastic collisions. The contribution from the diagrams such as in Fig.(c) however vanishes for a system with center of inversion symmetry ($d_{ii}=0$).

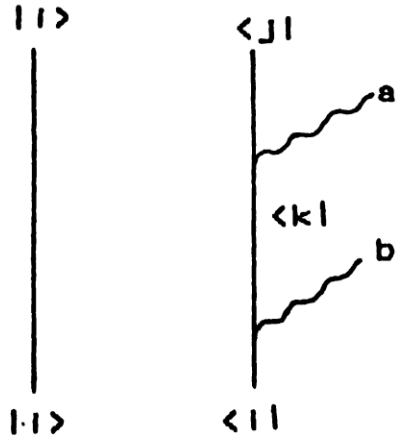
V. DIAGRAMMATIC CALCULATION OF $\chi^{(2)}$

In this section, we present a diagrammatic calculation of the second-order susceptibility $\chi^{(2)}$ of a multi-level system which is undergoing both elastic as well as inelastic collisions. The second-order susceptibility $\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)$ will be important for phenomena such as second harmonic generation in non-centrosymmetric media or in atomic systems in presence of symmetry-breaking electric fields. Further, $\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)$ can also be used to calculate the system observables such as the populations $\rho^{(2)}_{ii}$ and coherences $\rho^{(2)}_{ij}(i\neq j)$ by replacing d^{μ} in the expression by $|i\rangle\langle j|$, i.e., by replacing $d^{\mu}_{\alpha\beta}$ by $\delta_{\alpha i}\ \delta_{j\beta}$. The knowledge of the level

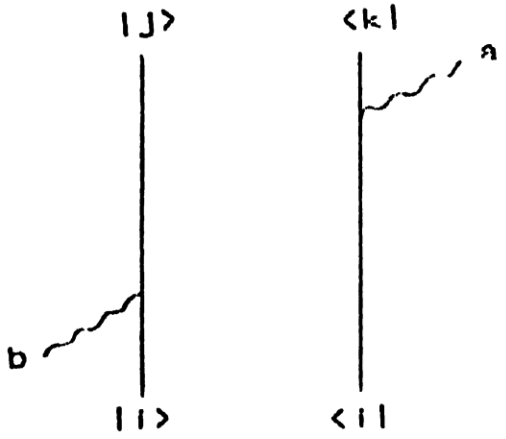
populations ($\rho^{(2)}_{ll}$) and coherences [$\rho^{(2)}_{lJ}$ $(l \neq J)$] is important in the calculation of fluorescence signals in systems undergoing both elastic and inelastic collisions. Note that a pressure-induced extra resonance (PIER) has been found to occur in fluorescence.[8,9] Hence the diagrams that we give below will be useful for analyzing phenomena such as are mentioned above. Consider a multilevel system interacting with two fields ω_1 and ω_2 whose cartesian components of polarization are α and β respectively. Then, the following diagrams determine the structure of the elastic contribution to $\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)$:



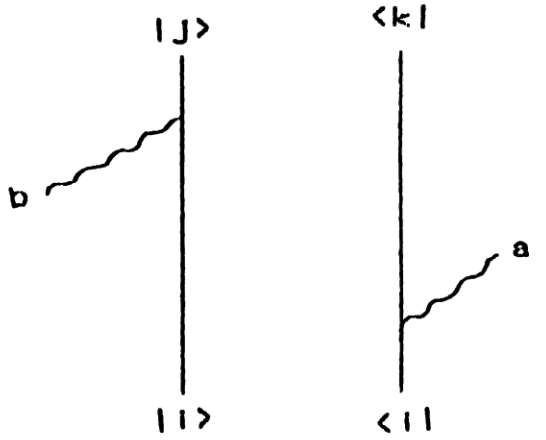
$$(-1)^2 \quad \frac{\rho^{(o)}_{ll} d^{\mu}_{lk} d^{\alpha}_{kJ} d^{\beta}_{Jl}}{(\omega_1+\omega_2-\Lambda_{kl})(\omega_2-\Lambda_{Jl})} \quad . \quad (D2.1)$$



$$(-1)^2 \quad \frac{\rho^{(o)}_{ll} d^{\mu}_{Jl} (-d^{\alpha}_{kJ})(-d^{\beta}_{lk})}{(\omega_1+\omega_2-\Lambda_{lJ})(\omega_2-\Lambda_{lk})} \qquad (D2.2)$$



$$(-1)^2 \frac{\rho^{(o)}_{ii} d^{\mu}_{kj} (-d^{\alpha}_{ik}) d^{\beta}_{ji}}{(\omega_1+\omega_2-\Lambda_{jk})(\omega_2-\Lambda_{ji})} \qquad (D2.3)$$



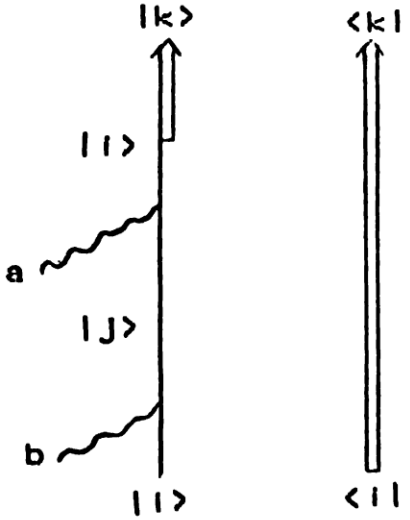
$$(-1)^2 \frac{\rho^{(o)}_{ii} d^{\mu}_{kj} (-d^{\alpha}_{ik}) d^{\beta}_{ji}}{(\omega_1+\omega_2-\Lambda_{jk})(\omega_1-\Lambda_{ik})} \quad . \qquad (D2.4)$$

Note that in the above diagrams a and b represent the two fields (ω_1,α) and (ω_2,β) respectively. One can obtain four more diagrams by interchanging the time order of interaction of the fields a and b in the diagrams (D2.1)-(D2.4). The corresponding terms can be obtained by interchanging (ω_1,α) and (ω_2,β) in the respective expressions on the right hand side in (D2.1)-(D2.4). Thus, these eight diagrams yield the elastic contribution to $\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)$. Note that in the diagrams in (D2.1) and (D2.2), the interactions are all on one side of the diagram. These are the so-called parametric diagrams. The non-parametric diagrams (D2.3) and (D2.4) for instance correspond to the two fields ω_b (on the |ket> side) and ω_a (on the <bra| side) interacting with the system in two different time orders. Note that such differently time-ordered

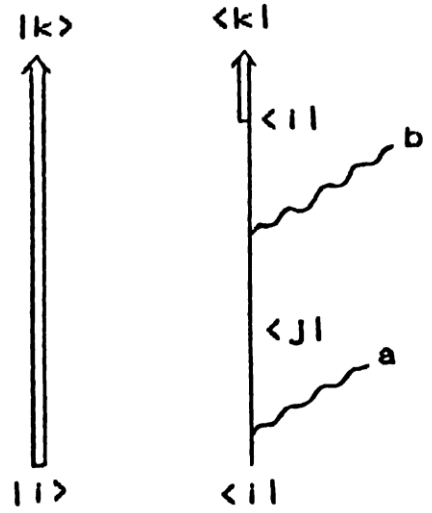
contributions, when combined, lead to a cancellation of the resonance $(\omega_1+\omega_2-\Lambda_{jk})^{-1}$ in the absence of collisions. Consider the case when there is no decay of population out of the system. Then, the total contribution from (D2.3) and (D2.4) is

$$T = (-1)^2 \frac{\rho^{(o)}_{ll} d^{\mu}_{kj} (-d^{\alpha}_{ik}) d^{\beta}_{jl}}{(\omega_2-\Lambda_{jl})(\omega_1-\Lambda_{ik})} \left[1 + \frac{\Lambda_{jk}-\Lambda_{jl}-\Lambda_{ik}}{\omega_1+\omega_2-\Lambda_{jk}} \right] . \qquad (3.16)$$

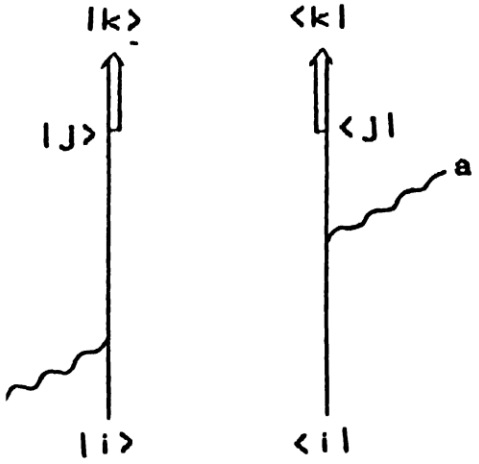
Thus, if $|l\rangle$ is the ground state (which is not decaying), then the coefficient of the resonance $(\omega_1+\omega_2-\Lambda_{jk})^{-1}$ in (3.16), $\Lambda_{jk}-\Lambda_{jl}-\Lambda_{ik} = -i(\Gamma_{jk}-\Gamma_{jl}-\Gamma_{ik})$ is non-zero only if phase-changing collisions are present ($\Gamma^{ph}_{\alpha\beta} \neq 0$). This is an example of the well-known pressure-induced extra resonance.[5] Note that the total contribution to the susceptibility of the multi-level system is obtained by summing over the indices i,j and k. Next we give the diagrams which yield the inelastic contributions to $\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2)$. These are



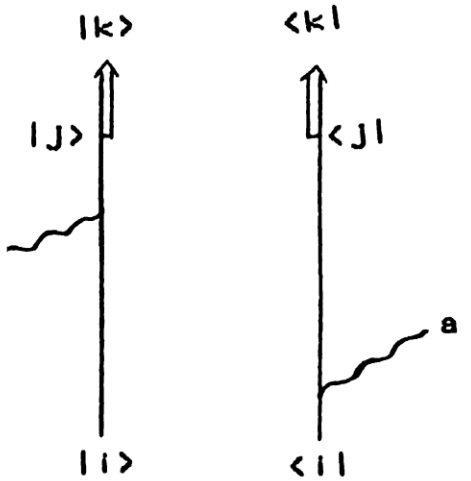
$$(-1)^2 \frac{\rho^{(o)}_{ll} d^{\mu}_{kk} d^{\alpha}_{lj} d^{\beta}_{jl}}{\omega_2-\Lambda_{jl}} C_{lk}(\omega_1+\omega_2) \quad . \qquad (D2.5)$$



$$(-1)^2 \frac{\rho^{(o)}_{ii} d^{\mu}_{kk} (-d^{\alpha}_{ij})(-d^{\beta}_{ji})}{\omega_1 - \Lambda_{ij}} C_{ik}(\omega_1+\omega_2) \quad . \tag{D2.6}$$



$$(-1)^2 \frac{\rho^{(o)}_{ii} d^{\mu}_{kk} (-d^{\alpha}_{ij}) d^{\beta}_{ji}}{\omega_2 - \Lambda_{ji}} C_{jk}(\omega_1+\omega_2) \quad . \tag{D2.7}$$



$$(-1)^2 \frac{\rho^{(o)}_{ii} d^{\mu}_{kk} (-d^{\alpha}_{ij}) d^{\beta}_{ji}}{\omega_1 - \Lambda_{ij}} C_{jk}(\omega_1+\omega_2) \quad . \tag{D2.8}$$

Again, one obtains four more diagrams (terms) by permuting the indices a and b in the diagrams (D2.5)-(D2.8) [permuting (ω_1,α) and (ω_2,β) in the respective terms on the right hand side in (D2.5)-(D2.8)]. Note that in the non-parametric diagrams (D2.7) and (D2.8), the fields a and b interact with the system in two different time orders. The combined contribution from these two diagrams is

$$T = (-1)^2 \frac{\rho^{(o)}_{ll} d^{\mu}_{kk} (-d^{\alpha}_{lJ}) d^{\beta}_{Jl}}{(\omega_2-\Lambda_{Jl})(\omega_1-\Lambda_{lJ})} \sum_{\ell}^{-} S^{-1}_{\ell J} S_{k\ell} \left[1 + \frac{i\lambda_\ell + 2i\Gamma_{lJ}}{\omega_1+\omega_2-i\lambda_\ell} \right] \tag{3.17}$$

Note that in writing (3.17), we have replaced $C_{Jk}(\omega_1+\omega_2)$ by $B_{Jk}(\omega_1+\omega_2)$ under the assumtion that there is no decay of population out of the system levels. Thus if one of the eigenvalues λ_ℓ of the population relaxation matrix R equals $-2\Gamma_{lJ}$, there is a cancellation of the resonant term $(\omega_1+\omega_2-i\lambda_\ell)^{-1}$ corresponding to that particular λ_ℓ. Hence the condition for the existence of the resonance at $\omega_1+\omega_2=0$ is that $\lambda_\ell+i\Gamma_{lJ}$ be non-zero for any one of the λ_ℓ. This is analogous to the condition $\Gamma_{Jk}-\Gamma_{Jl}-\Gamma_{lk} \neq 0$ in the elastic case [Eq.(3.16)]. Similarly, the combined contribution from the two parametric diagrams (D2.5) and (D2.6) (which correspond to two different time orders of the fields a and b) is

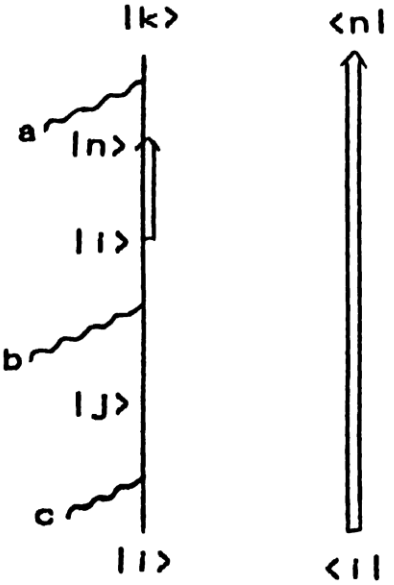
$$T = (-1)^2 \frac{\rho^{(o)}_{ll} d^{\mu}_{kk} d^{\alpha}_{lJ} d^{\beta}_{Jl}}{(\omega_2-\Lambda_{Jl})(\omega_1-\Lambda_{lJ})} \sum_{\ell}^{-} S^{-1}_{\ell l} S_{k\ell} \left[1 + \frac{i\lambda_\ell + 2i\Gamma_{lJ}}{\omega_1+\omega_2-i\lambda_\ell} \right]. \tag{3.18}$$

It is evident from (3.18) that if $\lambda_\ell+2i\Gamma_{lJ}\neq 0$ for some eigenvalue

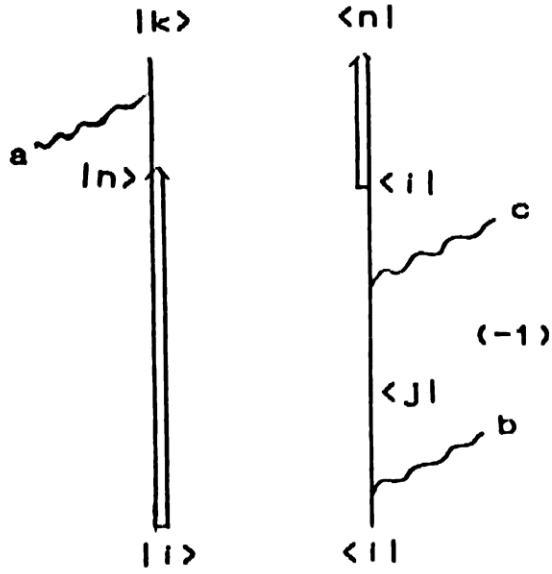
λ_ℓ of the population relaxation matrix R, then, even the parametric diagrams contribute the inelastic resonance at $\omega_1+\omega_2=0$. This is in contrast to the elastic case where only the non-parametric diagrams contribute to the pressure-induced extra resonance [Eq.(3.16)].

VI. DIAGRAMMATIC CALCULATION OF INELASTIC CONTRIBUTIONS TO $\chi^{(3)}$

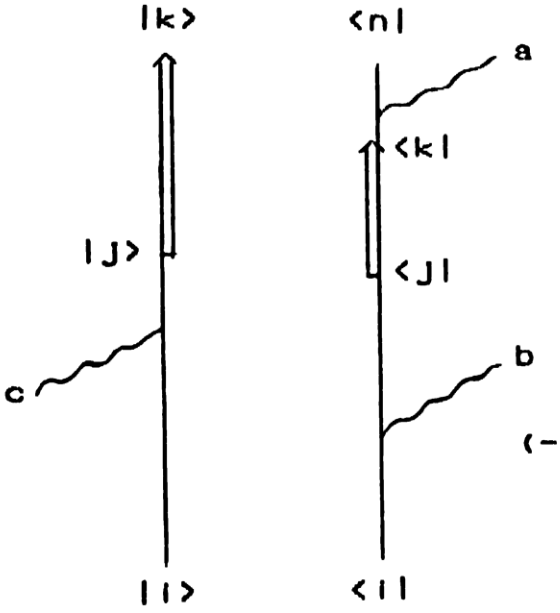
In this section, we present the diagrams which yield the contributions coming from the inelastic collisions, to the third-order susceptibility $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$ of a multi-level system. Such contributions, as we have shown in Chapter II, contain the additional resonant terms that arise due to the inelastic collisions. The following diagrams determine the structure of the inelastic contributions to $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$:



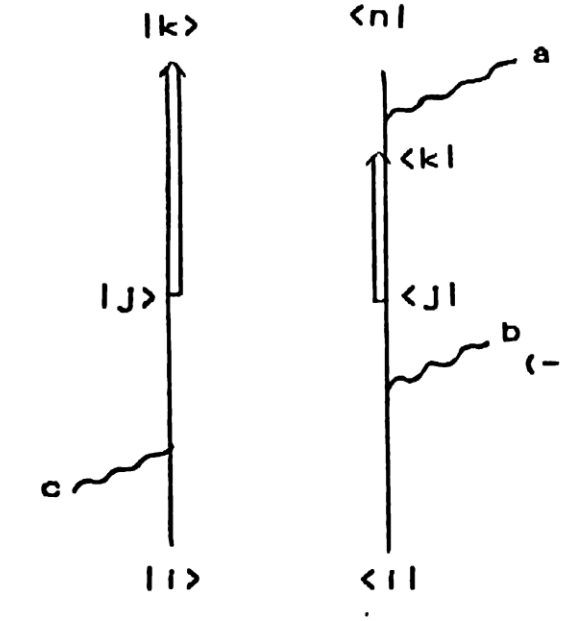
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nk} d^{\alpha}_{kn} d^{\beta}_{ij} d^{\gamma}_{jl}}{(\omega_p-\Lambda_{kn})(\omega_3-\Lambda_{jl})} C_{in}(\omega_2+\omega_3) \qquad \text{(D3.1)}$$



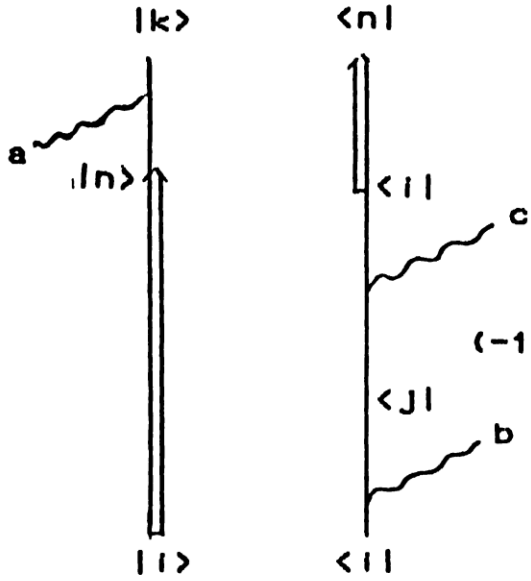
$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} d^{\alpha}_{kn} (-d^{\beta}_{ij})(-d^{\gamma}_{ji})}{(\omega_p - \Lambda_{kn})(\omega_2 - \Lambda_{ij})} C_{in}(\omega_2+\omega_3) \ . \qquad \text{(D3.6)}$$



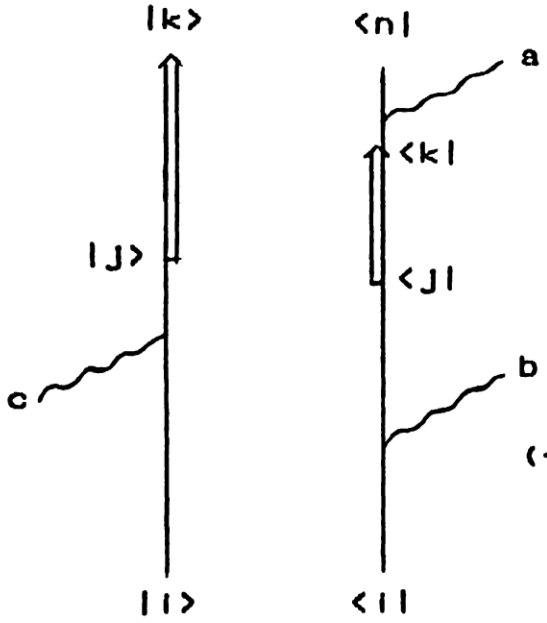
$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} (-d^{\alpha}_{kn}) d^{\gamma}_{ji} (-d^{\beta}_{ij})}{(\omega_p - \Lambda_{kn})(\omega_2 - \Lambda_{ij})} C_{jk}(\omega_2+\omega_3) \ . \qquad \text{(D3.7)}$$



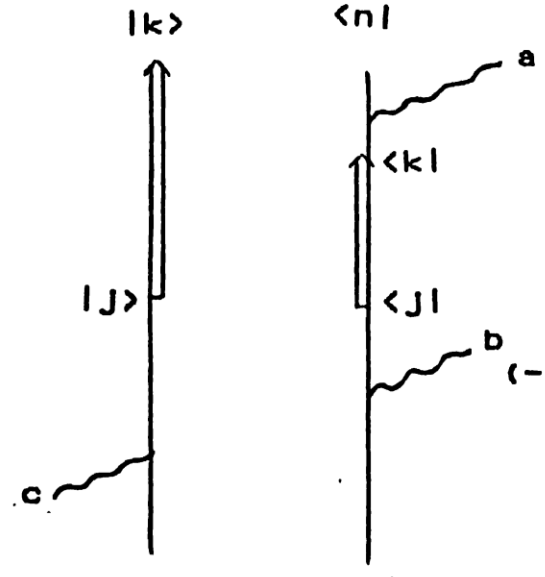
$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} (-d^{\alpha}_{kn}) d^{\gamma}_{ji} (-d^{\beta}_{ij})}{(\omega_p - \Lambda_{kn})(\omega_3 - \Lambda_{ji})} C_{jk}(\omega_2+\omega_3) \ . \qquad \text{(D3.8)}$$



$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} d^{\alpha}_{kn} (-d^{\beta}_{ij})(-d^{\gamma}_{ji})}{(\omega_p - \Lambda_{kn})(\omega_2 - \Lambda_{ij})} C_{in}(\omega_2+\omega_3) \quad . \tag{D3.6}$$



$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} (-d^{\alpha}_{kn}) d^{\gamma}_{ji} (-d^{\beta}_{ij})}{(\omega_p - \Lambda_{kn})(\omega_2 - \Lambda_{ij})} C_{jk}(\omega_2+\omega_3) \tag{D3.7}$$



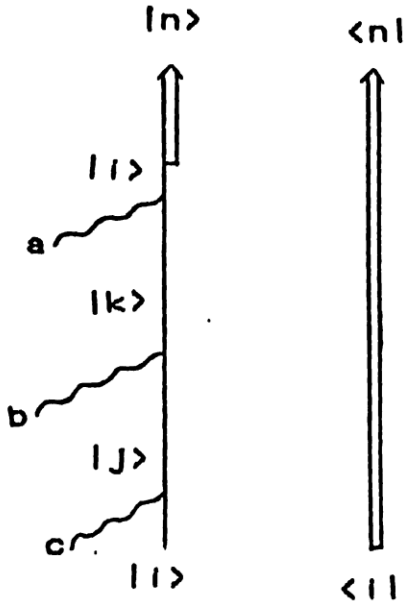
$$(-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{nk} (-d^{\alpha}_{kn}) d^{\gamma}_{ji} (-d^{\beta}_{ij})}{(\omega_p - \Lambda_{kn})(\omega_3 - \Lambda_{ji})} C_{jk}(\omega_2+\omega_3) \quad . \tag{D3.8}$$

In the above diagrams, a,b, and c denote the fields with frequencies ω_1, ω_2 and ω_3 and polarization indices α,β and γ respectively. By permuting a, b and c in the diagrams (D3.1)-(D3.8), one can write down 32 more such diagrams. The corresponding terms can be written down by permuting (ω_1,α), (ω_2,β) and (ω_3,γ) in the expressions on the right-hand side in (D3.1)-(D3.8). Thus in a system with center of inversion symmetry ($d_{ii}=0$), these 48 diagrams determine completely the structure of the inelastic contributions to $\chi^{(3)}$. Note that a cancellation of the resonance at $\omega_2+\omega_3=0$ can result when the diagrams (D3.1) and (D3.6) or (D3.2) and (D3.3) or (D3.4) and (D3.5) or (D3.7) and (D3.8) are combined, depending on the structure of the eigenvalues of the population relaxation matrix R. For instance, the combined contribution from the diagrams (D3.7) and (D3.8) is

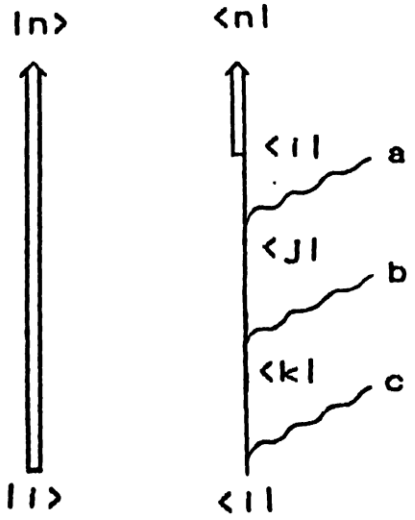
$$T = (-1)^3 \frac{\rho_{ii}^{(o)} d_{nk}^{\mu} (-d_{kn}^{\alpha}) d_{ji}^{\gamma} (-d_{ij}^{\beta})}{(\omega_p-\Lambda_{kn})(\omega_2-\Lambda_{ij})(\omega_3-\Lambda_{ji})} \sum_{\ell}^{-} S_{\ell j}^{-1} S_{k\ell} \left[1 + \frac{i\lambda_\ell+2i\Gamma_{ij}}{\omega_2+\omega_3-i\lambda_\ell} \right] , \tag{3.18}$$

in the case when there is no decay of population out of the system levels. Thus if $\lambda_\ell+2\Gamma_{ij}=0$ for some λ_ℓ, then the cancellation of the resonant term $(\omega_2+\omega_3-i\lambda_\ell)^{-1}$ results for that λ_ℓ. Otherwise the resonance at $\omega_2+\omega_3=0$, whose width $|\lambda_\ell|$ is determined by the inelastic collisions, is present in $\chi^{(3)}$.

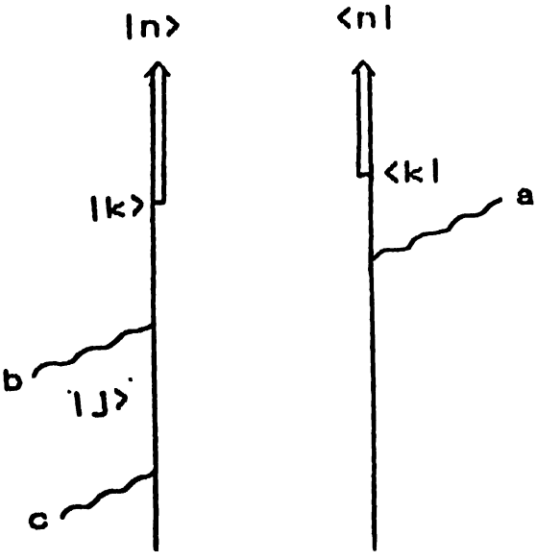
For a system without center of inversion symmetry ($d_{ll} \neq 0$), there are 48 more diagrams which contribute to the inelastic collision-induced terms in $\chi^{(3)}$. These are as follows:



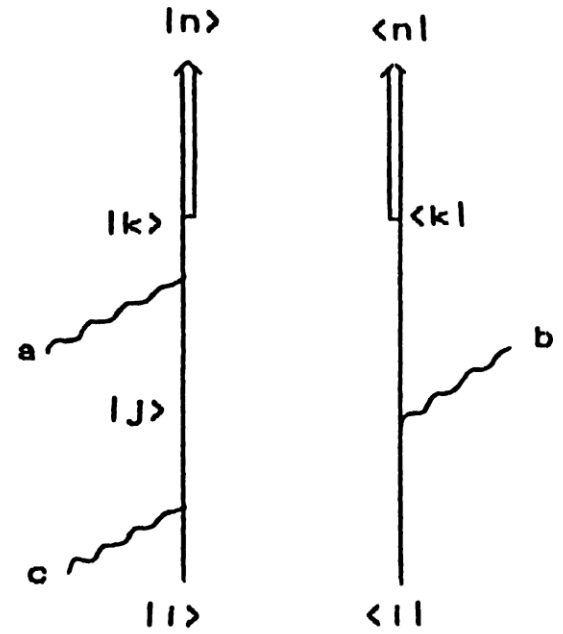
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} d^{\alpha}_{lk} d^{\beta}_{kJ} d^{\gamma}_{Jl}}{(\omega_2+\omega_3-\Lambda_{kl})(\omega_3-\Lambda_{Jl})} C_{in}(\omega_p), \qquad \text{(D3.9)}$$



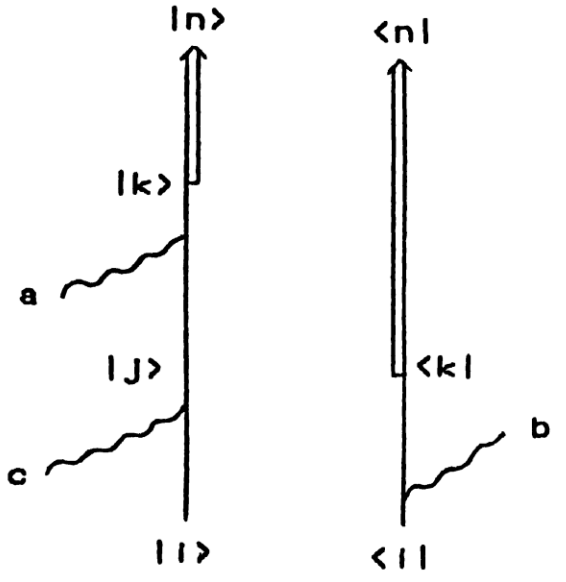
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} (-d^{\alpha}_{Jl})(-d^{\beta}_{kJ})(-d^{\gamma}_{lk})}{(\omega_2+\omega_3-\Lambda_{lJ})(\omega_3-\Lambda_{lk})} C_{in}(\omega_p) \qquad \text{(D3.10)}$$



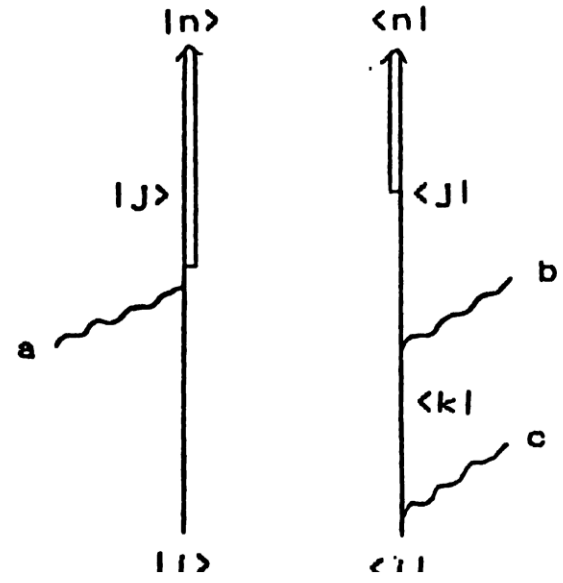
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} (-d^{\alpha}_{lk}) d^{\beta}_{kJ} d^{\gamma}_{Jl}}{(\omega_2+\omega_3-\Lambda_{kl})(\omega_3-\Lambda_{Jl})} C_{kn}(\omega_p) \qquad \text{(D3.11)}$$



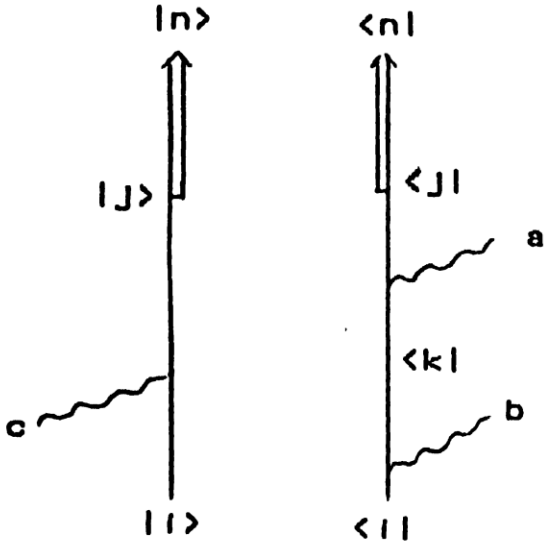
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} d^{\alpha}_{kJ} (-d^{\beta}_{lk}) d^{\gamma}_{Jl}}{(\omega_2+\omega_3-\Lambda_{Jk})(\omega_3-\Lambda_{Jl})} C_{kn}(\omega_p) \qquad \text{(D3.12)}$$



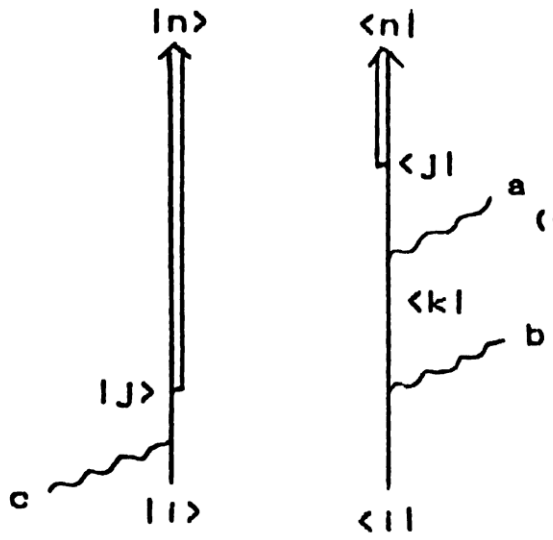
$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} d^{\alpha}_{kJ} (-d^{\beta}_{lk}) d^{\gamma}_{Jl}}{(\omega_2+\omega_3-\Lambda_{Jk})(\omega_2-\Lambda_{lk})} C_{kn}(\omega_p). \qquad \text{(D3.13)}$$



$$(-1)^3 \frac{\rho^{(o)}_{ll} d^{\mu}_{nn} (-d^{\beta}_{kJ}) d^{\alpha}_{Jl} (-d^{\gamma}_{lk})}{(\omega_2+\omega_3-\Lambda_{lJ})(\omega_3-\Lambda_{lk})} C_{Jn}(\omega_p) . \qquad \text{(D3.14)}$$



$$(-1)^3 \frac{\rho^{(o)}_{II} d^{\mu}_{nn} (-d^{\alpha}_{kJ}) d^{\gamma}_{JI} (-d^{\beta}_{Ik})}{(\omega_2+\omega_3-\Lambda_{Jk})(\omega_2-\Lambda_{Ik})} C_{Jn}(\omega_p) \qquad \text{(D3.15)}$$



$$(-1)^3 \frac{\rho^{(o)}_{II} d^{\mu}_{nn} (-d^{\alpha}_{kJ})(-d^{\beta}_{Ik}) d^{\gamma}_{JI}}{(\omega_2+\omega_3-\Lambda_{Jk})(\omega_3-\Lambda_{JI})} C_{Jn}(\omega_p) \, . \qquad \text{(D3.16)}$$

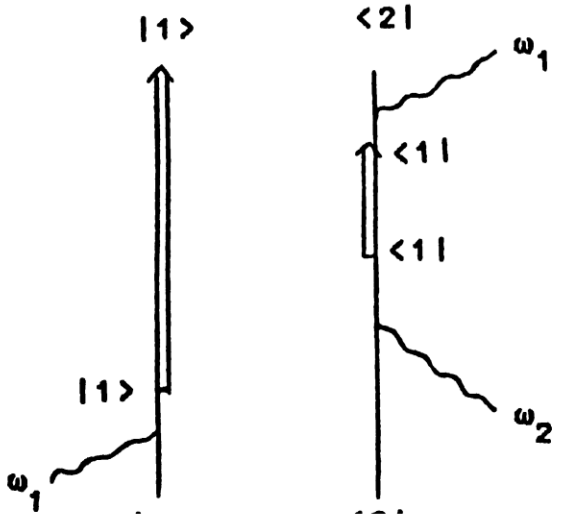
Again by permuting a,b, and c in the diagrams (D3.9)-(D3.16) [(ω_1,α), (ω_2,β) and (ω_3,γ) in the respective terms], one can obtain 32 more diagrams [terms]. Note that the term $(\omega_2+\omega_3-\Lambda_{Jk})^{-1}$ in (D3.12),(D3.13),(D3.15) and (D3.16) is the pressure-induced extra resonance which is present only in a system undergoing inelastic collisions, i.e., when $C_{Jn}(\omega)$ or $C_{kn}(\omega)\neq 0$. Note for instance that the combined contribution of the diagrams (D3.12) and (D3.13) [which correspond to different time orders of ω_2 and ω_3 photons] can lead to a cancellation of the resonant term $(\omega_2+\omega_3-\Lambda_{Jk})^{-1}$. On combining the terms in (D3.12) and (D3.13), we obtain,

$$T = (-1)^3 \frac{\rho_{11}^{(o)} d_{nn} d_{kJ}^{\alpha} (-d_{Ik}^{\beta}) d_{IJ}^{\gamma}}{(\omega_3 - \Lambda_{JI})(\omega_2 - \Lambda_{Ik})} C_{kn}(\omega_p) \left[1 + \frac{\Lambda_{Jk} - \Lambda_{JI} - \Lambda_{Ik}}{\omega_2 + \omega_3 - \Lambda_{Jk}} \right] . \tag{3.19}$$

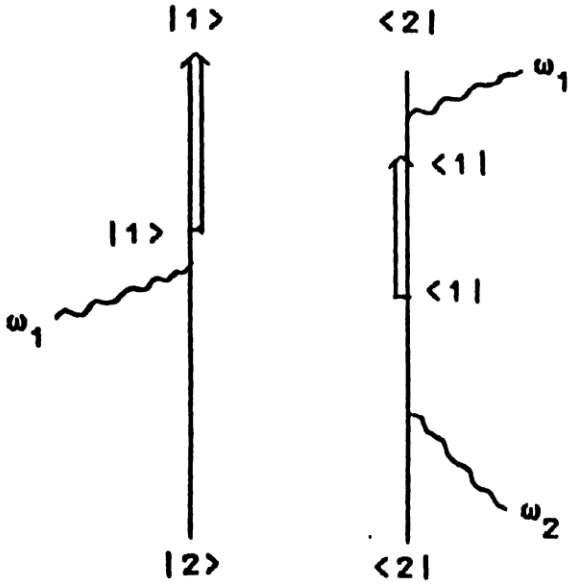
Thus the condition for the resonant term $(\omega_2+\omega_3-\Lambda_{Jk})^{-1}$ is that both $C_{kn}(\omega_p)$ and $\Lambda_{Jk}-\Lambda_{JI}-\Lambda_{Ik}\left[= -i(\Gamma_{Jk}-\Gamma_{JI}-\Gamma_{Ik})\right]$ be non-zero.

Diagrammatic calculation of the four-wave mixing susceptibility of ruby

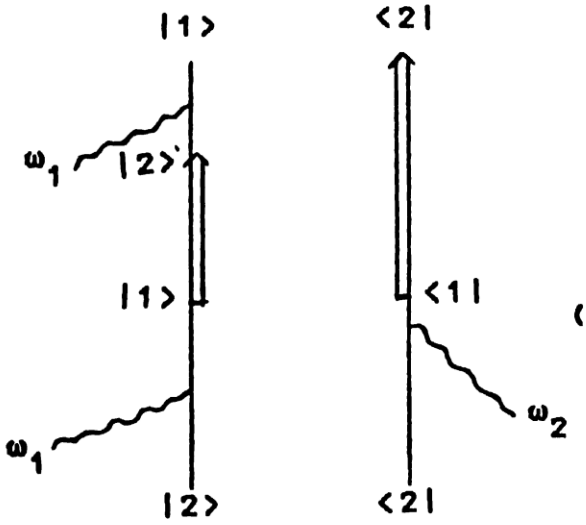
We illustrate the diagrammatic method discussed in the previous sections by calculating the four-wave mixing susceptibility of ruby which is modelled by a three-level system [see Fig. 2]. The levels $|1\rangle$ and $|2\rangle$ are connected by a dipole transition. For simplicity, we assume $\gamma_{12}=0$. Hence before application of the pump (ω_1) and probe (ω_2) fields, the system is in the ground state $|2\rangle$, i.e., $\rho_{22}^{(o)}=1$. The various inelastic rates γ_{IJ} are as given in Fig.2. In writing the diagrams, we consider resonant processes only. The diagrams which lead to resonant contributions to $\chi_{\mu\alpha\beta\gamma}^{(3)}(\omega_1,\omega_1,-\omega_2)$ are as given below.



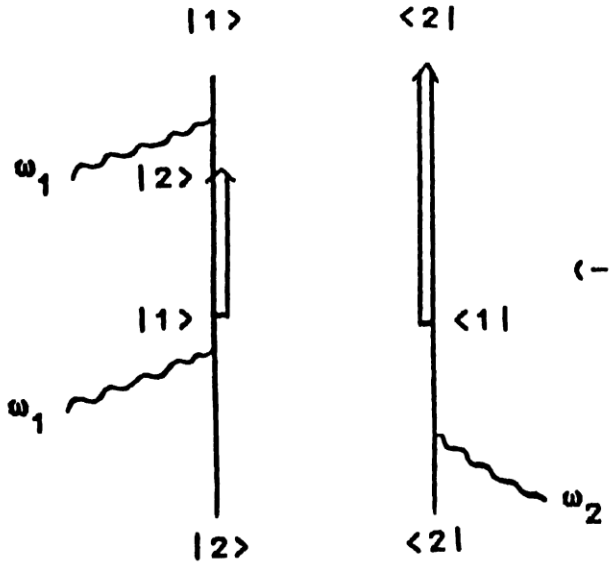
$$(-1)^3 \frac{2d_{21}^{\mu}(-d_{12}^{\alpha})(-d_{21}^{\gamma})d_{12}^{\beta}}{(\omega_1-\Lambda_{12})(2\omega_1-\omega_2-\Lambda_{12})} B_{11}(\omega_1-\omega_2) \tag{R.1}$$



$$(-1)^3 \frac{2d^{\mu}_{21}(-d^{\alpha}_{12})d^{\beta}_{12}(-d^{\gamma}_{21})}{(-\omega_2-\Lambda_{21})(2\omega_1-\omega_2-\Lambda_{12})} B_{11}(\omega_1-\omega_2) \qquad \text{(R.2)}$$



$$(-1)^3 \frac{2d^{\mu}_{21}d^{\alpha}_{12}d^{\beta}_{12}(-d^{\gamma}_{21})}{(\omega_1-\Lambda_{12})(2\omega_1-\omega_2-\Lambda_{12})} B_{12}(\omega_1-\omega_2) \qquad \text{(R.3)}$$



$$(-1)^3 \frac{2d^{\mu}_{21}d^{\alpha}_{12}d^{\beta}_{12}(-d^{\gamma}_{21})}{(-\omega_2-\Lambda_{21})(2\omega_1-\omega_2-\Lambda_{12})} B_{12}(\omega_1-\omega_2) \qquad \text{(R.4)}$$

Note that the evolution of the initial vector |2><2| in the diagram (R.1), for instance, can be schematically represented as

$$|2\rangle\langle 2| \longrightarrow |1\rangle\langle 2| \longrightarrow |1\rangle\langle 1| \Longrightarrow |1\rangle\langle 1| \longrightarrow |1\rangle\langle 2|$$

Since the level $|1\rangle$ is decaying, the vector $|1\rangle\langle 1|$ at two different times is different, and hence $|1\rangle\langle 1| \Longrightarrow |1\rangle\langle 1|$ must be taken as a relaxation-induced transition. Note that we have multiplied the terms in (R.1)-(R.4) by a factor of two because we get the same terms on interchanging (α,ω_1) and (β,ω_1). The information about the relaxation through the level $|3\rangle$ is contained in the matrix elements of B, namely

$$B_{11}(\omega) = \frac{1}{\omega+i(\gamma_{21}+\gamma_{31})} \quad ,$$

$$B_{12}(\omega) = -\frac{(1+A)}{\omega+i(\gamma_{21}+\gamma_{31})} + \frac{A}{\omega+i\gamma_{23}} \quad ,$$

$$A = \frac{\gamma_{31}}{(\gamma_{23}-\gamma_{21}-\gamma_{31})} \qquad (3.20)$$

Thus the four-wave mixing susceptibility $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_1,-\omega_2)$ of ruby is given by the sum of the contributions from the above four diagrams. Note that the expression for $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_1,-\omega_2)$ thus obtained agrees with the result given in Eq.(2.52) if we make the identification

$$C(\omega_1-\omega_2) = B_{11}(\omega_1-\omega_2) - B_{12}(\omega_1-\omega_2)$$

Note for instance that the diagrams in (R.1) and (R.2) correspond to two different time-orderings of the fields ω_1 and ω_2. On combining these two differently time-ordered contributions, we get

$$T = (-1)^3 \frac{2d^{\mu}_{21}(-d^{\alpha}_{12})d^{\beta}_{12}(-d^{\gamma}_{21})}{(2\omega_1-\omega_2-\Lambda_{12})(\omega_1-\Lambda_{12})(-\omega_2-\Lambda_{21})} \frac{(\omega_1-\omega_2-\Lambda_{12}-\Lambda_{21})}{\omega_1-\omega_2+i(\gamma_{21}+\gamma_{31})} . \tag{3.21}$$

In the absence of phase-changing collisions, $\Lambda_{12}+\Lambda_{21}=-2i\Gamma_{12}=-i(\gamma_{21}+\gamma_{31})$. Hence the resonace at $\omega_2=\omega_1$ in (3.21) cancels. Similarly, on combining the two differently time-ordered contributions in (R.3) and (R.4), we have

$$T = (-1)^3 \frac{2d^{\mu}_{21}d^{\alpha}_{12}d^{\beta}_{12}(-d^{\gamma}_{21})}{(2\omega_1-\omega_2-\Lambda_{12})(\omega_1-\Lambda_{12})(-\omega_2-\Lambda_{21})} \left[-1 - \frac{i\gamma_{31}}{\omega_1-\omega_2+i\gamma_{23}} \right] \tag{3.22}$$

Thus, in an open two-level system ($\gamma_{31}\neq 0$) the narrow resonance at $\omega_1-\omega_2$ with width γ_{23} is always present.

Thus, in conclusion, we have developed a diagrammatic method which enables us to determine the contributions to the nonlinear susceptibilities which arise due to the inelastic collisions. The diagrams that determine the inelastic contributions are different in structure from the usual diagrams. The corresponding terms too have a different structure. The rules for the translation of any particular inelastic diagram into the corresponding term in the expression for the nonlinear suscepti-

bility are derived from an analysis of the equivalence between the algebraic method of calculating such expressions and the method using the double-sided Feynman diagrams. A diagrammatic calculation of the elastic and the inelastic contributions to the second-order susceptibility is presented. A diagrammatic calculation of the inelastic contributions to the third-order susceptibility too is given. Just as the usual pressure-induced extra resonances, the additional resonances arising due to the inelastic collisions too are found to arise due to the non-cancellation of the contributions from two different different time orders in which the fields interact with the system.

CHAPTER IV

TRANSIENT RESPONSE OF COHERENTLY DRIVEN SYSTEMS

In Chapter II, we calculated the nonlinear susceptibilities describing the steady-state response of the system. The steady-state response is, for most systems, independent of the initial state. Thus, whatever the initial state may be, the response in the long time limit is what one would get if the system were initially in thermal equilibrium. However, quite often we are interested in monitoring the dynamics of a system as it relaxes towards a steady-state, after it is prepared in some particular initial state. Further, it has been recognized in recent years, that a combination of frequency-domain and time-domain methods can be more effective in extracting the maximum possible information about the dynamics of a system interacting with fields and undergoing relaxation.[31,53] In view of this, it is desirable to have a nonlinear response theory which enables us to calculate not only the detailed structure of the various resonances but also the detailed temporal evolution of each of the various processes. In this chapter, we generalize the formulation of Chapter II so that it is valid under arbitrary initial conditions and for all time-scales of interest. In Section II, we present a Liouville operator formulation of the nonlinear time-dependent response theory of a system undergoing arbitrary relaxation. The initial conditions are left arbitrary. The system could initially be in one of its energy

eigenstates or in a coherent superposition state. A compact expression for the nth order time-dependent nonlinear susceptibility $\chi^{(n)}$ is given. In Sections III-V, we give explicit expressions for time-dependent $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ respectively. In the long-time limit, these reduce to the steady-state expressions given in Chapter II. We present a number of applications of the various time-dependent χ's. These include applications to the beating phenomena, transient pump-probe experiments and new resonances in transient four-wave mixing.

II. NONLINEAR TRANSIENT SUSCEPTIBILITIES

Consider a quantum mechanical system prepared intially in a state $\rho^{(o)}(0)$, which is undergoing relaxation and which is interacting with external fields. The time evolution of such a sytem is described by the density matrix equation of motion

$$\frac{\partial \rho}{\partial t} = L_o\rho + L_f(t)\rho \qquad (4.1)$$

where the Liouville operator L_o[Eq. (2.3)] contains the effects of relaxation and $L_f(t) = -[H_f(t),]$, describes the interaction with the external fields. We examine the response of the system to n^{th} order in the external fields which are switched on at time t=0. Using standard perturbative methods [as explained in Chapter II, Eqs. (2.16)-(2.19)], one can write down an expression for the n^{th} order density matrix of the system initially prepared in the state $\rho^{(o)}(0)$.

$$\rho^{(n)}(t) = \int_0^t dt_1 \ldots \int_0^{t_{n-1}} dt_n \, e^{L_o(t-t_1)} L_f(t_1) \, e^{L_o(t_1-t_2)}$$

$$\times \; L_f(t_2) \ldots e^{L_o(t_{n-1}-t_n)} L_f(t_n) \, e^{L_o t_n} \rho^{(o)}(0) \quad . \qquad (4.2)$$

On making a change of variable $t-t_1 \rightarrow t_1$ in (4.2), we get

$$\rho^{(n)}(t) = \int_0^t dt_1 \int_0^{t-t_1} dt_2 \int_0^{t_2} dt_3 \ldots \int_0^{t_{n-1}} dt_n \, e^{L_o t_1} L_f(t-t_1) \, e^{L_o(t-t_1-t_2)}$$

$$\times L_f(t_2) \, e^{L_o(t_2-t_3)} \ldots L_f(t_n) \, e^{L_o t_n} \rho^{(o)}(0) \quad , \qquad (4.3)$$

which on letting $t-t_1-t_2 \rightarrow t_2$, becomes

$$\rho^{(o)}(t) = \int_0^t dt_1 \int_0^{t-t_1} dt_2 \int_0^{t-t_1-t_2} dt_3 \int_0^{t_3} dt_4 \ldots \int_0^{t_{n-1}} dt_n \, e^{L_o t_1} L_f(t-t_1) e^{L_o t_2}$$

$$\times \; L_f(t-t_1-t_2) \, e^{L_o(t-t_1-t_2-t_3)} L_f(t_3) \, e^{L_o(t_3-t_4)}$$

$$\ldots L_f(t_n) e^{L_o t_n} \rho^{(o)}(0) \qquad (4.4)$$

By changing variables in the above manner n times, Eq. (4.4) can be written in the form

$$\rho^{(n)}(t) = \int_0^t dt_1 \int_0^{t-t_1} dt_2 \cdots \int_0^{t-\sum_{l=1}^{n-1} t_l} dt_n \; e^{L_o t_1} L_f(t-t_1) \, e^{L_o t_2} \cdots e^{L_o t_n}$$

$$\times \; L_f\Big(t - \sum_{l=1}^{n} t_l\Big) \, e^{L_o\left(t - \sum_{l=1}^{n} t_l\right)} \rho^{(o)}(0) \quad . \tag{4.5}$$

Next, on introducing the Fourier transform of $H_f(t)$, $L_f(t)$, i.e.,

$$H_f\Big(t - \sum_{l=1}^{k} t_l\Big) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_l \; e^{-i\omega_l\left(t - \sum_{l=1}^{n} t_l\right)} H_f(\omega_l) \; ,$$

$$L_f\Big(t - \sum_{l=1}^{k} t_l\Big) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_l \; e^{-i\omega_l\left(t - \sum_{l=1}^{n} t_l\right)} L_f(\omega_l) \; ,$$

$$i = 1, 2, \ldots, n \tag{4.6}$$

in Eq. (4.5) and using the convolution theorem for the Laplace transforms, one obtains the result

$$\rho^{(n)}(t) = \Big(\frac{1}{2\pi}\Big)^n \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_n \; e^{-it \sum_{l=1}^{n} \omega_l} \Big(\frac{1}{2\pi i}\Big) \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} dz \; e^{zt}$$

$$\times \; (iz + \sum_{l=1}^{n} \omega_l - iL_o)^{-1} L_f(\omega_1) \, (iz + \sum_{l=2}^{n} \omega_l - iL_o)^{-1} L_f(\omega_2)$$

$$\ldots \; (iz + \omega_n - iL_o)^{-1} L_f(\omega_n) \, (iz - iL_o)^{-1} \rho^{(o)}(0) \tag{4.7}$$

Using Eq. (4.7) the n^{th} order nonlinear time-dependent response of the observable Q becomes

$$\times \mathrm{Tr}\Big\{ Q(iz + \sum_{i=1}^{n} \omega_i - iL_o)^{-1} L_{\alpha_1} (iz + \sum_{i=2}^{n} \omega_i - iL_o)^{-1} L_{\alpha_2}$$

$$\ldots (iz + \omega_n - iL_o)^{-1} L_{\alpha_n} (iz - iL_o)^{-1} \rho^{(o)}(0) \quad ,$$

$$L_{\alpha_n} = - [s_{\alpha_n}, \ ] \quad . \tag{4.11}$$

Here the symbol 'sym' implies that the right-hand side has to be symmetrized with respect to all the indices (ω_i, α_i) [see the discussion following Eq. (2.26)]. For the dipole Hamiltonian, $s_\alpha = d^\alpha$, $f_\alpha = E_\alpha$, where d^α, E_α are the α^{th} components respectively of the dipole moment operator and the electric field, the n^{th} order transient induced polarization is

$$P_\alpha^{(n)}(t) = \mathrm{Tr}\big(\rho^{(n)}(t) d^\alpha \big)$$

$$= \sum \Big(\frac{1}{2\pi} \Big)^n \int_{-\infty}^{\infty} d\omega_1 \ldots \int_{-\infty}^{\infty} d\omega_n \, e^{-it \sum_{i=1}^{n} \omega_i}$$

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}, t) \, E_{\alpha_1}(\omega_1) \ldots E_{\alpha_n}(\omega_n) \quad , \tag{4.12}$$

where

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}, t) = N(-i)^n \, \underline{\mathrm{sym}} \, \Big(\frac{1}{2\pi i} \Big) \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} dz \, e^{zt}$$

$$\mathrm{Tr}\Big\{ d^\alpha (iz + \sum_{i=1}^{n} \omega_i - iL_o)^{-1} L_{\alpha_1} (iz + \sum_{i=2}^{n} \omega_i - iL_o)^{-1} L_{\alpha_2}$$

$$\ldots (iz + \omega_n - iL_o)^{-1} L_{\alpha_n} (iz - iL_o)^{-1} \rho^{(o)}(0) \Big\} \quad ,$$

$$\times \mathrm{Tr}\Big\{ Q(iz + \sum_{i=1}^{n} \omega_i - iL_o)^{-1} L_{\alpha_1} (iz + \sum_{i=2}^{n} \omega_i - iL_o)^{-1} L_{\alpha_2}$$

$$\ldots (iz + \omega_n - iL_o)^{-1} L_{\alpha_n} i(z - iL_o)^{-1} \rho^{(o)}(0) \quad ,$$

$$L_{\alpha_n} = - [s_{\alpha_n}, \ ] \quad . \tag{4.11}$$

Here the symbol 'sym' implies that the right-hand side has to be symmetrized with respect to all the indices (ω_i, α_i) [see the discussion following Eq. (2.26)]. For the dipole Hamiltonian, $s_\alpha = d^\alpha$, $f_\alpha = E_\alpha$, where d^α, E_α are the α^{th} components respectively of the dipole moment operator and the electric field, the n^{th} order transient induced polarization is

$$P_\alpha^{(n)}(t) = \mathrm{Tr}\left(\rho^{(n)}(t) d^\alpha \right)$$

$$= \sum \left(\frac{1}{2\pi} \right)^n \int_{-\infty}^{\infty} d\omega_1 \ldots \int_{-\infty}^{\infty} d\omega_n \, e^{-it \sum_{i=1}^{n} \omega_i}$$

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}, t) \, E_{\alpha_1}(\omega_1) \ldots E_{\alpha_n}(\omega_n) \quad , \tag{4.12}$$

where

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}, t) = N(-i)^n \frac{\mathrm{sym}}{n!} \left(\frac{1}{2\pi i} \right) \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} dz \, e^{zt}$$

$$\mathrm{Tr}\Big\{ d^\alpha (iz + \sum_{i=1}^{n} \omega_i - iL_o)^{-1} L_{\alpha_1} (iz + \sum_{i=2}^{n} \omega_i - iL_o)^{-1} L_{\alpha_2}$$

$$\ldots (iz + \omega_n - iL_o)^{-1} L_{\alpha_n} i(iz - iL_o)^{-1} \rho^{(o)}(0) \Big\} \quad ,$$

$$L_\alpha \equiv -i[d^\alpha \quad , \quad] \tag{4.13}$$

where N is the atomic number density. Equation (4.13) is our general expression for the transient nonlinear response of a system. Note that one obtains the steady-state $\chi^{(n)}$ [Eq. (2.30)] by taking the contribution from the z=0 pole above in Eq. (4.13). If one writes

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\},t) \equiv \sum_J F_J \, e^{z_J t} \tag{4.14}$$

where the z_J's are the poles of the integrand in (4.13) and the F_J's are the corresponding residues, then the Fourier transform of the induced polarization can be expressed as

$$P^{(n)}_\alpha(\omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t} \, P^{(n)}_\alpha(t)$$

$$\sum_J F_J \, \delta(\omega - \sum_{i=1}^{n} \omega_i - iz_J) \tag{4.15}$$

Thus it is clear from Eq. (4.15) that while the nonlinear mixing described by the steady-state susceptibility $\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\})$ leads to generation of radiation at the frequency $\omega = \sum_{i=1}^{n} \omega_i$, the nonlinear mixing described by the time-dependent susceptibility $\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\},t)$ leads to generation of radiation at frequencies $\omega_J = \sum_{i=1}^{n} \omega_i + iz_J$, J=1,2,..., where the z_J's are the poles of the integrand in the expression (4.13). Note that in general, the z_J's consist of combinations of the field as well as the atomic frequencies. The equation (4.13) can also be written in the form

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\},t) = M^{(n)}(t) \left\{ \bar{\chi}^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}) \right\} \tag{4.16}$$

where we have defined

$$\bar{\chi}^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\}) = N s\nu \frac{\mathcal{A}^{!}}{n!} \mathrm{Tr} \left\{ d^{\alpha} \Big(\sum_{i=1}^{n} \omega_i - iL_o \Big)^{-1} L_{\alpha_1} \right.$$

$$\left. \times \Big[\sum_{i=2}^{n} \omega_i - iL_o \Big]^{-1} L_{\alpha_2} \cdots (\omega_n - iL_o)^{-1} L_{\alpha_n} \bar{\rho}^{(o)}(0) \right\},$$

$$\bar{\rho}^{(o)}(0) = i(-iL_o)^{-1} \rho^{(o)}(0) \tag{4.17}$$

Here $M^{(n)}(t)$ is a prescription for the modification of the $\bar{\chi}^{(n)}$'s as a result of the Laplace inversion in Eq. (4.13). The explicit action of the operator $M^{(n)}(t)$ on the product of resonant denominators is given by

$$M^{(n)}(t) \left\{ \frac{1}{\Delta_o \Delta_1 \cdots \Delta_n} \right\} = \frac{1}{2\pi i} \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} \frac{e^{zt}}{(iz+\Delta_o)(iz+\Delta_1)\cdots(iz+\Delta_n)}$$

$$= \frac{e^{i\Delta_o t}}{i(\Delta_1-\Delta_o)\cdots(\Delta_n-\Delta_o)} + \frac{e^{i\Delta_1 t}}{i(\Delta_o-\Delta_1)(\Delta_2-\Delta_1)\cdots(\Delta_n-\Delta_1)}$$

$$+ \cdots + \frac{e^{i\Delta_n t}}{i(\Delta_1-\Delta_n)(\Delta_2-\Delta_n)\cdots(\Delta_{n-1}-\Delta_n)} \tag{4.18}$$

The Δ's which occur in the $\bar{\chi}^{(n)}$'s have the form $\Delta_k = \sum_{\ell=1}^{k} \omega_\ell - \Lambda$, $k=1,2,..,n$; where Λ for instance could be the complex atomic frequency such as $\Lambda_{ij}(=\omega_{ij}-i\Gamma_{ij})$ or it could be equal to $i\lambda_\ell$, where λ_ℓ is an eigenvalue of the population relaxation matrix R. Δ_o is the denominator coming from $\bar{\rho}^{(o)}(0)$[Eq.(4.17)] which does not involve any laser frequency. The steady-state expression (2.30) is recovered from (4.16) and (4.17) on setting $M^{(n)}(t) \equiv 1$ and $\bar{\rho}^{(o)}(0) = \rho^{(o)}(\rho^{(o)}_{ij} = \delta_{ij}\rho^{(o)}_{ii})$. Often one is interested in the transient nonlinear response of a system that is initially in thermal equilibrium. In this case, $\bar{\rho}^{(o)}(0)$ has the simple form $i\rho^{(o)}/\Delta_o, \Delta_o=0$. Hence in this case one can write

$$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\},t) = m^{(n)}(t)\left\{\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\})\right\} \qquad (4.19)$$

where the $\chi^{(n)}$ in the curly bracket in (4.19) is the steady-state $\chi^{(n)}$ given by Eq. (2.30). The prescription $m^{(n)}(t)$ is

$$m^{(n)}(t)\left\{\frac{1}{\Delta_1\Delta_2\ldots\Delta_n}\right\} = \frac{1}{\Delta_1\Delta_2\ldots\Delta_n} - \left\{\frac{e^{i\Delta_1 t}}{\Delta_1(\Delta_2-\Delta_1)\ldots(\Delta_n-\Delta_1)}\right.$$

$$\left. + \ldots + \frac{e^{i\Delta_n t}}{\Delta_n(\Delta_1-\Delta_n)\ldots(\Delta_{n-1}-\Delta_n)}\right\} \qquad (4.20)$$

Note that the Δ_i's which appear in (4.20) are the resonant denominators that occur in the steady-state $\chi^{(n)}$[Eq. (2.30)]. Thus it is clear from (4.20) that for a system initially in thermal

equilibrium, the transient response will consist of terms which become resonant when any two resonant denominators that occur in the steady-state response become equal. This suggests the possibility of new resonances occuring in the transient response. These resonances could have very narrow linewidths since $Im(\Delta_i)\neq 0$ for all i. An interesting situation arises when $Im(\Delta_i)=Im(\Delta_j)$ for some Δ_i,Δ_j so that a resonance at $\Delta_i-\Delta_j=0$ with a width solely determined by the interaction time results. In Chapter V, we investigate this point in much detail by examining the transient four-wave mixing signals in a few model systems. Note that even in the case of an initially-prepared system, the transient response contains resonant terms such as $(\Delta_i-\Delta_j)^{-1}$ where the Δ_i,Δ_j now are the denominators in the expression for $\bar{\chi}^{(n)}$ [Eq. (4.17)]. As we have remarked earlier, in the transient case, coherent emission can occur at combinations of field as well as atomic frequencies. More specifically, the transient susceptibility $\chi^{(n)}(\{\omega_n\},t)$ gives rise to terms in $P^{(n)}(t)$ that oscillate with frequencies $\sum_{i=1}^{n}\omega_i+\Omega_j$, where Ω_j are all possible denominators that occur in $\bar{\chi}^{(n)}(\{\omega_n\})$ Hence if one is looking at the response at the frequency $\sum_{i=1}^{n}\omega_i$, or at frequencies in the neighbourhood of this frequency, then one should retain only those terms in $\chi^{(n)}(\{\omega_n\},t)$ that oscillate as $e^{i\Omega_j t}$, where $\Omega_j \ll$ a laser frequency. This can be ensured, for instance, by retaining only the terms with resonant denominators in $\bar{\chi}^{(n)}$. For instance, the Ω_j may correspond to a vibrational or a rotational frequency, as is the case in the various kinds of beats[28-30,54] or in the context of the transient methods of suppression of the non-resonant background[55] in coherent antistokes

Raman scattering (CARS) signals. In subsequent sections, we discuss various physical phenomena that can be described using the nonlinear response (4.13).

III. LINEAR TRANSIENT RESPONSE OF A COHERENTLY PREPARED SYSTEM

In this section, we specialize the result of Section II to obtain the explicit form of the transient linear response of a system. Such a linear response, as we will see, can be used to explain a class of beating phenomena as well as the transient pump-probe experiments.

Using (2.38) in (4.13), we get for the first-order time-dependent response

$$\chi^{(1)}_{\mu\alpha}(\omega,t) = M^{(1)}(t) \left\{ \bar{\chi}^{(1)}_{\mu\alpha}(\omega) \right\} \tag{4.21}$$

where

$$\bar{\chi}^{(1)}_{\mu\alpha}(\omega) = N \sum_{ijm} \bar{\rho}^{(o)}_{im}(0) \left\{ \frac{d^{\alpha}_{mj} d^{\mu}_{ji}}{\omega-\Lambda_{ij}} - \frac{d^{\mu}_{mj} d^{\alpha}_{ji}}{\omega-\Lambda_{jm}} + d^{\alpha}_{mi} d^{\mu}_{jj} \left[C_{ij}(\omega) - C_{mj}(\omega) \right] \right\} \tag{4.22}$$

$$\bar{\rho}^{(o)}_{im}(0) = i(1-\delta_{im})(-\Lambda_{im})^{-1} \rho^{(o)}_{im}(0) + i\delta_{im} \sum_{\ell} B_{\ell i}(0)\, \rho^{(o)}_{\ell\ell}(0) \tag{4.23}$$

Note that the action of $M^{(1)}(t)$ on the resonant denominators is given by

$$M^{(1)}(t)\left\{\frac{1}{\Delta_o\ \Delta_1}\right\} = \frac{e^{i\Delta_o t}}{i(\Delta_1-\Delta_o)} + \frac{e^{i\Delta_1 t}}{i(\Delta_o-\Delta_1)} \qquad (4.24)$$

For a system with centre of inversion symmetry ($d_{ii}=0$), the expression (4.21) can be written in the form

$$\chi^{(1)}_{\mu\alpha}(\omega,t) = \Psi^{(1)}_{\mu\alpha}(\omega,t) + \bar{\Phi}^{(1)}_{\mu\alpha}(\omega,t) \qquad (4.25)$$

where

$$\Psi^{(1)}_{\mu\alpha}(\omega,t) = N \sum_{ijm}^{-} \rho^{(o)}_{im}(0)\ (1-\delta_{im})\ e^{-i\Lambda_{im}t}$$

$$\left[d^{\alpha}_{mj} d^{\mu}_{ji} \left(\frac{1-e^{i(\omega-\Lambda_{ij}+\Lambda_{im})t}}{\omega-\Lambda_{ij}+\Lambda_{im}} \right) - d^{\mu}_{mj} d^{\alpha}_{ji} \left(\frac{1-e^{i(\omega-\Lambda_{jm}+\Lambda_{im})t}}{\omega-\Lambda_{jm}+\Lambda_{im}} \right) \right] \qquad (4.26)$$

and

$$\bar{\Phi}^{(1)}_{\mu\alpha}(\omega,t) = N \sum_{ijk\ell}^{-} S^{-1}_{k\ell}\ S_{ik}\ \rho^{(o)}_{\ell\ell}(0)\ e^{\lambda_k t}$$

$$\left[d^{\alpha}_{ij} d^{\mu}_{ji} \left(\frac{1-e^{i(\omega-\Lambda_{ij}+i\lambda_k)t}}{\omega-\Lambda_{ij}+i\lambda_k} \right) - d^{\mu}_{ij} d^{\alpha}_{ji} \left(\frac{1-e^{i(\omega-\Lambda_{ji}+i\lambda_k)t}}{\omega-\Lambda_{ji}+i\lambda_k} \right) \right] \qquad (4.27)$$

We have thus separated two distinct contributions to the transient response. These contributions arise from initial population

distributions ($\Phi^{(1)}$) and from initial coherences ($\Psi^{(1)}$) i.e., from the nonvanishing of the off-diagonal elements of the density matrix.

A. Beats produced by a coherently prepared system

Consider the transient response of a system whose initial state is such that there exists coherence between two nearby levels, i.e., $\rho_{im}^{(o)}(0)\neq 0$ for $i\neq m$. This will be the case when the initial state is prepared by the excitation by a coherent pulse of radiation. Equation (4.26) then has a term proportional to $e^{-i\Lambda_{im}t}$. This gives rise to beats at a frequency equal to the level spacing between two levels $|i\rangle$ and $|m\rangle$ not connected by a dipole transition. These two levels may correspond to Zeeman or hyperfine levels. The other time-dependent terms in Eq. (4.26) oscillate very rapidly for $\omega-\omega_{ij}>>\omega_{im}$, $\omega-\omega_{jm}>>\omega_{im}$, and hence will be unimportant. Such beats are obviously important for times $\Gamma_{im}t<<1$; $\omega_{im}>>\Gamma_{im}$. Note that Eq. (4.26) leads to both ground state and excited state beats.[30]

B. Transient pump-probe experiments

We would like to remark that in some cases, the pump-probe experiments can be described as a linear response of a coherently prepared system to the probe, provided the pump is switched off before the probe response is monitored. The pump (or the pump and the probe together, if they have been applied simultaneously)

creates the coherence (for example two-photon coherence] between two levels not connected by a dipole transition. The probe field can then monitor such a two-photon coherence by examining the field radiated as a function of time t.[53] A different situation obtains if the probe rather than the pump is switched off. The subsequent evolution of the system, then, is described by the linear response of the pump which is still on. Such a technique is used, for instance, to pick up only the Raman contribution to the coherent antistokes Raman scattering signal.[55] Consider for instance a Λ-type three-level system interacting with a pump (ω_ℓ) and a probe (ω_s) applied at t=0. The probe is then switched off at $t=\tau$. The linear response to the pump for times $t>\tau$ is given by Eqs. (4.26)-(4.27) with initial conditions at $t=\tau$ prepared by the pump and the probe. Note that only $\rho_{23}^{(o)}(\tau)$ contains the Raman resonance $(\omega_\ell-\omega_s-\Lambda_{23})^{-1}$. Hence the contribution to the pump response that is proportional to $\rho_{23}^{(o)}(\tau)$ can be computed from Eq. (4.26) and is given by

$$\chi_R^{(1)}(\omega_\ell,t) \propto - \rho_{23}^{(o)}(\tau) \left[\frac{e^{-i\Lambda_{23}(t-\tau)} - e^{i(\omega_\ell-\Lambda_{12})t}}{\omega_\ell-\Lambda_{12}+\Lambda_{23}} \right] \qquad (4.28)$$

Note that $\rho_{23}^{(o)}(\tau)$ has a spatial dependence $e^{i(\vec{k}_\ell-\vec{k}_s).\vec{r}}$. Hence it is clear from Eq. (4.26) that the induced polarization $P^{(1)}(t)$ for $t>\tau$ will have a term oscillating as $e^{i(2\vec{k}_\ell-\vec{k}_s).\vec{r}}$. However, it will have a frequency dependence $e^{-i(2\omega_\ell-\omega_s)t}$ only if $\Lambda_{23}=\omega_\ell-\omega_s$ (the other oscillating term in Eq. (4.26) is unimportant if the detuning $\omega_\ell-\omega_{12}>>\omega_{23}$). Thus, only the (Raman) resonant terms contribute to the light scattered in the direction $2\vec{k}_\ell-\vec{k}_s$.

IV. SECOND-ORDER TRANSIENT RESPONSE

In this section, we give the complete expression for the second-order response of a coherently prepared system. This can be used, for example, to study questions like the growth of the second harmonic radiation, the generation of radiation with input pump pulses. Another area where the second-order response is very useful is in connection with transient fluorescence measurements.

Using Eq. (2.38) in (4.13), we find the explicit form of the second-order time-dependent susceptibility to be

$$\chi^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2,t) = \frac{1}{2!} M^{(2)}(t)\left[\bar{\chi}^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) + (\alpha,\omega_1) \leftrightarrow (\beta,\omega_2)\right], \tag{4.29}$$

where

$$\bar{\chi}^{(2)}_{\mu\alpha\beta}(\omega_1,\omega_2) = N \sum_{ijnm} \bar{\rho}^{(0)}_{im}(0)$$

$$\Bigg\{ d_{mj}d_{jn}d_{ni}\left[\frac{\mu\alpha\beta}{(\omega_1+\omega_2-\Lambda_{jm})(\omega_2-\Lambda_{nm})} + \frac{\alpha\beta\mu}{(\omega_1+\omega_2-\Lambda_{in})(\omega_1-\Lambda_{ij})} \right.$$

$$\left. - \frac{\alpha\mu\beta}{\omega_1+\omega_2-\Lambda_{nj}}\left(\frac{1}{\omega_1-\Lambda_{ij}} + \frac{1}{\omega_2-\Lambda_{nm}} \right) \right] + \frac{d^{\mu}_{nj}d^{\alpha}_{jn}d^{\beta}_{mi}}{\omega_1+\omega_2-\Lambda_{jn}} [C_{mn}(\omega_2)-C_{mj}(\omega_2)$$

$$- C_{in}(\omega_2) + C_{ij}(\omega_2)] + \frac{d^{\mu}_{jj}d^{\alpha}_{mn}d^{\beta}_{ni}}{\omega_{-}-\Lambda_{nm}} [C_{mj}(\omega_1+\omega_2)-C_{nj}(\omega_1+\omega_2)]$$

$$- \frac{d^{\mu}_{jj} d^{\beta}_{mn} d^{\alpha}_{ni}}{\omega_2 - \Lambda_{in}} [C_{nj}(\omega_1+\omega_2) - C_{ij}(\omega_1+\omega_2)] \Big\} \qquad (4.30)$$

The operator $M^{(2)}$ is defined by

$$M^{(2)}(t)\left\{ \frac{1}{\Delta_o\ \Delta_1\ \Delta_2} \right\} = \frac{e^{i\Delta_o t}}{i(\Delta_1-\Delta_o)(\Delta_2-\Delta_o)} + \frac{e^{i\Delta_1 t}}{i(\Delta_o-\Delta_1)(\Delta_2-\Delta_1)}$$

$$+ \frac{e^{i\Delta_2 t}}{i(\Delta_o-\Delta_2)(\Delta_1-\Delta_2)} \qquad (4.31)$$

In the following, we discuss some important examples of second-order response.

Transient Fluorescence

Laser-excited fluorescence studies essentially require the knowledge of the populations of various excited states to second order in the external field. Using the formulation of Section II, the population $N_i(t)$ of the i^{th} level will be

$$N_i(t) = \sum_{\alpha\beta} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2\ e^{-i(\omega_1+\omega_2)t}\ N^{(2)}_{i\alpha\beta}(\omega_1,\omega_2,t) E_{\alpha}(\omega_1) E_{\beta}(\omega_2)\ , \qquad (4.32)$$

where $N^{(2)}_{i\alpha\beta}(\omega_1,\omega_2,t)$ can be obtained from Eq. (3.23),(3.24) if we replace d^{μ} (but not d^{α} and d^{β}) by the operator $|i\rangle\langle i|$.

Beats in Fluorescence with Excited-State Coherences

Consider the simple case where a system is prepared initially in a coherent superposition of excited levels $|2\rangle$ and $|3\rangle$, say by excitation with an intense ps pulse. Then the absorption to a higher level $|1\rangle$ is given by $N_1(t)$ which can be calculated to second order in the applied field of frequency ω_ℓ. Using Eqs.(4.23),(4.29) and (4.30) we get

$$N_1(t) = M^{(2)}(t) \left\{ \frac{i\rho_{23}^{(0)}(0)}{-\Lambda_{23}} \left[\frac{d_{31}^{\alpha} d_{12}^{\beta} (B_{31}(0)-B_{32}(0))}{\omega_\ell - \Lambda_{13}} \right.\right.$$

$$\left.\left. \frac{d_{31}^{\beta} d_{12}^{\alpha} (B_{11}(0)-B_{21}(0))}{-\omega_\ell - \Lambda_{21}} \right] + (2 \leftrightarrow 3) \right\} \qquad (4.33)$$

where the B terms are as defined in (2.34). Thus the use of the prescription in $M^{(2)}(t)$ in (4.33) will give rise to a term oscillating as $e^{-i\Lambda_{23}t}$, apart from other terms. This corresponds to the beats at the frequency ω_{23}. In particular in the radiative relaxation case, when the applied field is detuned far from the optical transitions, $N_1(t)$ has a simple structure

$$N_1(t) \propto \frac{e^{-\gamma t}}{\Delta^2} \left[\cos \omega_{23} t + e^{-\gamma t} \right] \qquad (4.34)$$

where γ is the rate of decay from $|1\rangle$ to $|2\rangle[|3\rangle]$ and Δ is the detuning. This explains the well-known quantum beats in absorption from excited state coherences.[29]

V. THIRD-ORDER TRANSIENT RESPONSE

We next use the general formulation of Section II to obtain the form of the third-order time-dependent susceptibility $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3,t)$. Such a susceptibility can be used to describe a number of spectroscopic situations. For example, the susceptibility $\chi^{(3)}(\omega_1,-\omega_1,\omega_2,t)$ will give the time-development of the Raman signal at ω_2 produced by a pump field of frequency ω_1. Such a time development is important in distinguishing between resonant Raman scattering and fluorescence.[56,57] In general, susceptibilities like $\chi^{(3)}(\omega_1,\omega_2,\omega_3,t)$ are useful in time-resolved frequency-resolved spectroscopy.[31]

The explicit expression for the time-dependent $\chi^{(3)}$ can be obtained by using (2.38) in (4.13). We quote the result without proof:

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2\omega_3,t) = \frac{M^{(3)}(t)}{3!}\left\{ \bar{\chi}^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + \text{five permutations}\right.$$

$$\begin{bmatrix} \alpha & \beta & \gamma \\ \omega_1 & \omega_2 & \omega_3 \end{bmatrix} \longrightarrow \begin{bmatrix} \alpha & \gamma & \beta \\ \omega_1 & \omega_3 & \omega_2 \end{bmatrix}, \begin{bmatrix} \beta & \alpha & \gamma \\ \omega_2 & \omega_1 & \omega_3 \end{bmatrix}$$

$$\begin{bmatrix} \beta & \gamma & \alpha \\ \omega_2 & \omega_1 & \omega_3 \end{bmatrix}, \begin{bmatrix} \gamma & \alpha & \beta \\ \omega_3 & \omega_1 & \omega_2 \end{bmatrix}$$

$$\left.\begin{bmatrix} \gamma & \beta & \alpha \\ \omega_3 & \omega_2 & \omega_1 \end{bmatrix}\right\} \qquad (4.35)$$

We express $\bar{\chi}^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$ as a sum of several distinct types of contributions

$$\bar{\chi}^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) + E^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) \quad . \quad (4.36)$$

Here $B^{(3)}$, $C^{(3)}$, $D^{(3)}$ and $E^{(3)}$ are given by

$$B^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = N \sum_{lnkjm} \bar{\rho}^{(0)}_{lm}(0)$$

$$\left\{ d_{mn}d_{nk}d_{kj}d_{jl} \left[\frac{\gamma\beta\alpha\mu}{(\omega_p-\Lambda_{lj})(\omega_2+\omega_3-\Lambda_{lk})(\omega_3-\Lambda_{ln})} - \right.\right.$$

$$- \frac{\mu\gamma\beta\alpha}{(\omega_p-\Lambda_{nm})(\omega_2+\omega_1-\Lambda_{km})(\omega_1-\Lambda_{jm})} + \frac{\gamma\mu\beta\alpha}{(\omega_p-\Lambda_{kn})} \left(\frac{1}{(\omega_2+\omega_1-\Lambda_{km})(\omega_1-\Lambda_{jm})} \right.$$

$$\left. + \frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_1-\Lambda_{jm})} + \frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_3-\Lambda_{in})} \right)$$

$$- \frac{\gamma\beta\mu\alpha}{(\omega_p-\Lambda_{jk})} \left(\frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_3-\Lambda_{in})} + \frac{1}{(\omega_1+\omega_3-\Lambda_{jn})(\omega_1-\Lambda_{jm})} \right.$$

$$\left.\left. \left. + \frac{1}{(\omega_2+\omega_3-\Lambda_{lk})(\omega_3-\Lambda_{ln})} \right) \right] \right\} \quad (4.37)$$

$$C^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = N \sum^{-}_{lnkjm} \bar{\rho}^{(o)}_{lm}(0)\ \frac{d^{\mu}_{kn} d^{\alpha}_{nk} d^{\gamma}_{mj} d^{\beta}_{jl}}{\omega_p - \Lambda_{nk}}$$

$$\times \left[\frac{A_1(\omega_2+\omega_3)}{\omega_2-\Lambda_{jm}} + \frac{A_2(\omega_2+\omega_3)}{\omega_3-\Lambda_{lj}} \right]$$

$$A_1(\omega) \equiv C_{mn}(\omega) - C_{jn}(\omega) - C_{mk}(\omega) + C_{jk}(\omega) \quad ,$$

$$A_2(\omega) \equiv C_{in}(\omega) - C_{jn}(\omega) - C_{ik}(\omega) + C_{jk}(\omega) \qquad (4.38)$$

$$D^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = N \sum^{-}_{lnkjm} \bar{\rho}^{(o)}_{lm}(0)\ d^{\alpha}_{mn} d^{\beta}_{nk} d^{\gamma}_{kl} d^{\mu}_{jj}$$

$$\times \left[\frac{(C_{nj}(\omega_p) - C_{mj}(\omega_p))}{(\omega_2+\omega_3-\Lambda_{nm})(\omega_3-\Lambda_{km})} + \frac{(C_{lj}(\omega_p) - C_{kj}(\omega_p))}{(\omega_2+\omega_1-\Lambda_{lk})(\omega_1-\Lambda_{ln})} \right.$$

$$\left. - \frac{(C_{kj}(\omega_p) - C_{nj}(\omega_p))}{\omega_1+\omega_3-\Lambda_{kn}} \left(\frac{1}{\omega_1-\Lambda_{ln}} + \frac{1}{\omega_3-\Lambda_{km}} \right) \right] \qquad (4.39)$$

and

$$E^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2\omega_3) = N \sum^{-}_{lnkjm} \bar{\rho}^{(o)}_{lm}(0)\ d^{\gamma}_{ml} d^{\alpha}_{nk} d^{\beta}_{kn} d^{\mu}_{jj}$$

$$\times \frac{(C_{kj}(\omega_p) - C_{nj}(\omega_p)) A_3(\omega_3)}{(\omega_2+\omega_3-\Lambda_{kn})} \quad ,$$

$$A_3(\omega) \equiv C_{ik}(\omega) - C_{in}(\omega) - C_{mk}(\omega) + C_{mn}(\omega) \quad . \quad (4.40)$$

In Eqs. (4.37)-(4.40) we have set $\omega_p \equiv \omega_1+\omega_2+\omega_3$. Note that $D^{(3)}$ and $E^{(3)}$ are zero for a centrosymmetric medium ($d_{ll}=0$). Thus Eqs.(4.35)-(4.40) constitute the complete result for the third-order transient response of a system that is prepared initially in one of the eigenstates or in a superposition state.

In conclusion, we have developed a formulation of the transient nonlinear response of a system undergoing arbitrary relaxation and interacting with external fields. The theory is valid under arbitrary initial preparation of the system and for all time-scales of interest. For a system initially in thermal equilibrium, the expressions for the transient susceptibilities to various orders in the weak fields can be obtained by using a prescription for modifying the terms in the corresponding steady-state expressions. The general structure suggests the possibility of the existence of new and possibly narrow resonances in the transient nonlinear response. Explicit expressions for the first, second and third-order transient susceptibilities are obtained. These expressions account for various transient phenomena such as beats, and these are useful in transient four-wave mixing and transient pump-probe experiments.

CHAPTER V

NEW RESONANCES IN TRANSIENT NONLINEAR SPECTROSCOPY

An important point that emerged from the formulation of transient response in the previous chapter was that for a system initially in thermal equilibrium, the resonances that occur in the transient response have the structure $(\Delta_i-\Delta_J)^{-1}$, where $\Delta_i^{-1},\Delta_J^{-1}$ $(i\neq J)$ themselves are the resonances that occur in the steady-state response. Hence new and possibly also narrow resonances (since $\text{Im}\ \Delta_i>0$ for all i) could occur in the transient response. A very interesting situation arises when $\text{Im}\Delta_i=\text{Im}\Delta_J$, in which case the contribution from the relaxation effects to the width of a resonance like $(\Delta_i-\Delta_J)^{-1}$ vanishes. The width of such a resonance is then determined essentially by the time-duration of the interaction between the system and the fields. Thus in the transient domain one can see very interesting coherence effects like resonances between two initially unpopulated states. These new types of 'extra' resonances are always present in the transient nonlinear response of systems and they exist even in the absence of collisional[5] and saturation effects.[11] In this chapter, we discuss in detail the existence of such extra resonances in transient four-wave mixing (FWM) in the context of model two and three-level systems thus covering many of the systems which have been traditionally used for the studies of the pressure-induced extra resonances (PIER).

Consider the transient FWM signal produced by a system interacting with either cw fields or long pulses. Consider the system to be intially in thermal equilibrium. As we have shown in Chapter IV [Eqs.(4.13),(4.14)], the transient susceptibility $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3,t)$ of a system initially in thermal equilibrium can be obtained from the steady-state susceptibility as follows:

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3,t) = m^{(3)}(t)\left\{\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)\right\} , \qquad (5.1)$$

where $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$ is the steady-state third-order susceptibility and the operation $m^{(3)}(t)$ stands for

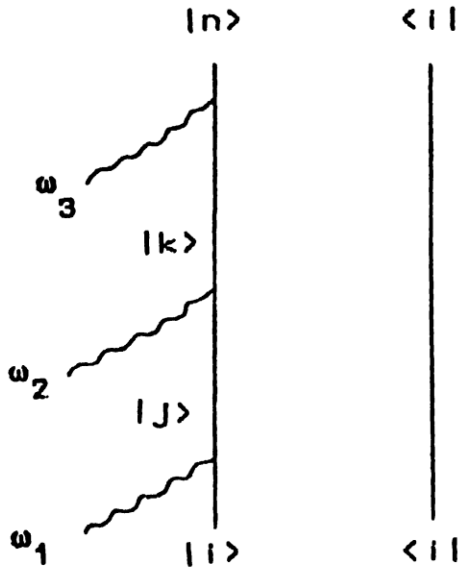
$$m^{(3)}(t)\left\{\frac{1}{\Delta_1\Delta_2\Delta_3}\right\} = \frac{1}{\Delta_1\Delta_2\Delta_3} - \left\{\frac{e^{i\Delta_1 t}}{\Delta_1(\Delta_2-\Delta_1)(\Delta_3-\Delta_1)} + \frac{e^{i\Delta_2 t}}{\Delta_2(\Delta_1-\Delta_2)(\Delta_3-\Delta_2)} + \frac{e^{i\Delta_3 t}}{\Delta_3(\Delta_1-\Delta_3)(\Delta_2-\Delta_3)}\right\} . \qquad (5.2)$$

The quantities Δ_1,Δ_2 and Δ_3 are the resonant denominators that occur in any particular term in $\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)$. The existence of the 'new' resonances can be seen by considering a typical term in $\chi^{(3)}$. For example consider the term

$$X(\omega) = (-1)^3 \frac{\rho^{(o)}_{ii} d^{\mu}_{in} d^{\gamma}_{nk} d^{\beta}_{kj} d^{\alpha}_{ji}}{(\omega_p-\Lambda_{ni})(\omega_1+\omega_2-\Lambda_{ki})(\omega_1-\Lambda_{ji})} ,$$

$$\omega_p = \omega_1+\omega_2+\omega_3 , \quad \Lambda_{ij} \equiv \omega_{ij} - i\Gamma_{ij} \qquad (5.3)$$

in the steady-state response. Note that such a term corresponds to the following double-sided diagram:



On using the prescription (5.2), the corresponding term in the transient response will be

$$X(t) = (-1)^3 \rho_{ii}^{(o)} d_{in}^{\mu} d_{nk}^{\gamma} d_{kJ}^{\beta} d_{Ji}^{\alpha}$$

$$\times \left[\frac{1}{(\omega_p - \Lambda_{ni})(\omega_1+\omega_2-\Lambda_{ki})(\omega_1-\Lambda_{Ji})} \right.$$

$$- \frac{e^{i(\omega_p-\Lambda_{ni})t}}{(\omega_p-\Lambda_{ni})(\omega_3-\omega_{nk}+i\Gamma_{nik})(\omega_2+\omega_3-\omega_{nJ}+i\Gamma_{niJ})}$$

$$+ \frac{e^{i(\omega_1+\omega_2-\Lambda_{ki})t}}{(\omega_1+\omega_2-\Lambda_{ki})(\omega_3-\omega_{nk}+i\Gamma_{nik})(\omega_2-\omega_{kJ}+i\Gamma_{kiJ})}$$

$$\left. - \frac{e^{i(\omega_1-\Lambda_{Ji})t}}{(\omega_1-\Lambda_{Ji})(\omega_2+\omega_3-\omega_{nJ}+i\Gamma_{niJ})(\omega_2-\omega_{kJ}+i\Gamma_{kiJ})} \right]$$

$$\Gamma_{nik} \equiv \Gamma_{ni} - \Gamma_{ik} \qquad (5.4)$$

Note that the relaxation parameter Γ_{ij} is associated with the ij^{th} element of the density matrix, as in the relaxation model of Bloembergen et al.[5] The expression (5.4) already shows the existence of the extra resonances in transient response even if collisional dephasing is absent. The second and fourth terms can lead to a resonance between two unpopulated states when $\omega_2+\omega_3=\omega_{nj}$ This resonance has a relaxation-induced width $\Gamma_{nij}=\Gamma_{ni}-\Gamma_{ij}$ which can be zero if $\Gamma_{ni}=\Gamma_{ij}$. Similarly, the first and third terms lead to resonances of the form $\omega_1+\omega_2=0$ if the levels $|k\rangle$ and $|i\rangle$ are the same. Thus the result (5.1) for the transient four-wave mixing response establishes the existence of different types of extra resonances in transient experiments. However note that these new resonances are not 'induced' by any external mechanism but are always present in the transient response of a system. Hence these should be contrasted with those induced by pressure of the buffer gas,[5-7] source fluctuations,[58] or due to strong pumps.[59] We next present the results of our calculations on the transient four-wave mixing signals produced by several model systems. We present numerical results and the approximate form of the signals which enables us to understand the numerical results.

A. Transient FWM from a two-level system:

Consider an experiment in which the generation of the FWM

signal is monitored at different times. The system under consideration is shown in Fig.1 where we put $\gamma_{12}=0$. The generated signal is in the direction $2\vec{k}_\ell-\vec{k}_s$, where $\vec{k}_\ell$ and $\vec{k}_s$ refer respectively to the wave vectors of the pump and the probe. Such a signal is proportional to $|\vec{P}(t)|^2$ where $\vec{P}(t)$ is the induced polarization. Hence to second order in the pump and to first order in the probe, the transient FWM signal will be given by

$$S(t) \propto |\chi^{(3)}(\omega_\ell, \omega_\ell, -\omega_s, t)|^2 \qquad (5.5)$$

where the transient FWM susceptibility $\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s,t)$ is determined from the steady-state susceptibility by using the prescription (5.1)-(5.2). For a two-level system, the steady-state susceptibility is given by

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s) = -\frac{2N}{3!}\frac{|d_{12}|^4}{(2\omega_\ell-\omega_s-\Lambda_{12})(\omega_\ell-\omega_s+i\gamma_{21})}\left[\frac{1}{\omega_\ell-\Lambda_{12}}+\frac{1}{-\omega_s-\Lambda_{21}}\right]. \qquad (5.6)$$

We have dropped the tensorial indices in Eqs.(5.5)-(5.6) under the assumption that all fields are similarly polarized. Note that the term $(\omega_\ell-\omega_s+i\gamma_{21})^{-1}$ in (5.6) is the usual pressure-induced extra resonance, which survives only if $\Gamma_{12}^{ph} \neq 0$. On using the prescription (5.1)-(5.2) the transient FWM susceptibility will have the following structure:

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s,t) = -\frac{2N}{3!}|d_{12}|^4\frac{1}{(\omega_\ell-\omega_s)}$$

$$\left[\frac{e^{i(2\omega_\ell-\omega_s-\Lambda_{12})t}}{(2\omega_\ell-\omega_s-\Lambda_{12})(\omega_\ell-\Lambda_{12}-i\gamma_{21})}-\frac{e^{i(\omega_\ell-\Lambda_{12})t}}{(\omega_\ell-\Lambda_{12})(\omega_s-\Lambda_{12}-i\gamma_{21})}\right]$$

+ other terms (5.7)

The 'other terms' in (5.7) refer to the terms that do not contain the resonance $(\omega_\ell-\omega_s)^{-1}$. Note that the expression in (5.7) does not blow up when $\omega_\ell=\omega_s$ due to the fact that the coefficient of the term $(\omega_\ell-\omega_s)^{-1}$ becomes zero when $\omega_\ell=\omega_s$, and hence the zeroes in the denominator and numerator cancel. This is in contrast to what obtains in the case of the usual resonances, for instance, the PIER $(\omega_\ell-\omega_s+i\gamma_{21})^{-1}$ in (5.6). Another point of contrast is that while the usual extra resonance $(\omega_\ell-\omega_s+i\gamma_{21})^{-1}$ in the FWM signal arises due to the component in the induced polarization oscillating with frequency $2\omega_\ell-\omega_s$, the new resonance $(\omega_\ell-\omega_s)^{-1}$ arises due to the combined contribution of two components oscillating with a frequency difference of $|\omega_\ell-\omega_s|$. Note further that the new resonance $(\omega_\ell-\omega_s)^{-1}$ is 'transient' in the sense that it does not survive in the long-time limit. This can be seen from (5.7) since $Im(\Lambda_{12})=-\Gamma_{12}<0$. Moreover, the width of the resonance $(\omega_\ell-\omega_s)^{-1}$ has no contribution from relaxation processes and hence it is essentially determined by the time of interaction t. In the case when the fields are detuned far away from resonance, i.e., $|\omega_\ell-\omega_{12}|\sim|\omega_s-\omega_{12}|\sim\Delta \gg T_1^{-1},T_2^{-1}$, the transient FWM signal (defined by Eq.(5.5)) has a simple structure[2]

$$S(t) \propto \frac{(\gamma_{21}t)^2 e^{-\gamma_{21}t}}{\Delta^4} \frac{\sin^2(\Omega t/2)}{(\Omega t/2)^2}, \quad \Omega = \omega_\ell-\omega_s ,$$

$$\gamma_{21} = 2T_2^{-1} \tag{5.8}$$

The terms that are ignored in (5.8) are of higher order in Δ. The usual steady-state extra resonance produced by dephasing collisions is of the order of $1/\Delta^6$. Thus the transient FWM signal is quite significant. The results for various times of observation are shown in Fig.6. This figure shows the well-defined extra resonance at $\omega_\ell = \omega_s$ for different times of observation. The width of the resonance is determined by the time of observation. The signal goes to zero for very long times and thus these resonances do not survive in the steady-state unless we include collisions with a buffer gas. The approximate result (5.8) explains the numerical results of Fig.6 [which have been obtained using the full expression for the transient FWM signal] very well. Note that the signal [(5.5)-(5.7) or (5.8)] is affected by residual Doppler broadening. However, under suitable experimental conditions, the residual Doppler width can be made small enough so that it does not affect the observability of the transient resonance. For example in Na, for the pump-probe angle[45] $\theta = 0.3^o$, the residual Doppler width $\Delta_r \left(= \frac{\omega}{C} \sqrt{\frac{KT}{M}} \sin\theta\right)$ is about 5.74 MHz at room temperature. Hence if we monitor the system on a time-scale 10^{-8}-10^{-9} sec., then the residual Doppler width is much smaller compared to the observation time width ($\sim t^{-1}$) and hence can be neglected. Thus it is desirable to choose times of interest to be smaller than the typical decay times. It is of course possible to make the pump-probe angle still smaller which would reduce the residual Doppler width and measurements can be made at larger time-scales. Note that we do not monitor the decay of coherence, and

hence the experimental situation envisaged above is in the same class of experiments as that of, say, Bai et al.[61]

B. Transient FWM in ruby

We next demonstrate the extra resonances in transient FWM signal produced from ruby. Systems like ruby have been extensively studied.[45] The system can be modelled as a three-level system with various relaxation rates as shown in Fig.2. Here we assume $\gamma_{12}=0$, $\rho_{22}^{(o)}=1$. We have already calculated the steady-state FWM susceptibility in Chapter II [Eq.(2.57)]. This has essentially the same structure as that for the two-level system, but for the extra term proportional to γ_{31} [see Eq.(2.57)]. The transient FWM susceptibility for ruby can be easily obtained from (2.57) by using the prescription (5.1)-(5.2). Note that in ruby the parameters $\gamma_{21},\gamma_{31},\gamma_{23}$ differ considerably[44] [$\gamma_{31}=2\times10^{7}$/sec, $\gamma_{21}=3\times10^{5}$/sec, $\gamma_{23}=10^{3}/3$/sec] and hence we can examine the signal at different time-scales. Obviously the transient signal would be much smaller at the largest time-scale (γ_{23}^{-1}) of the system. Thus in Fig.7 we show the signal on the smallest time-scale ($\approx\gamma_{31}^{-1}$). The transient signal shows the well- defined extra resonance with a width of the order of 1/t. The calculated signal agrees well with the approximate formula (5.8) with $\gamma_{21}\rightarrow\gamma_{21}+\gamma_{31}$. The signal on the time-scale γ_{21}^{-1} is also quite significant though smaller than the signal on the scale γ_{31}^{-1}.

C. Transient Hanle Resonance in FWM

We next show how a transient Hanle resonance can be produced in four-wave mixing. Consider a three-level system as shown in Fig.3. Let the levels $|1\rangle$ and $|2\rangle$ decay radiatively to the level $|3\rangle$ at the rate γ. The levels $|1\rangle$ and $|2\rangle$ are the Zeeman levels corresponding to $J=1$, $m = \pm 1$. The level $|3\rangle$ corresponds to $J=0$, $m=0$. For the sake of illustration we assume a phase conjugation geometry for the fields (the transient Hanle resonances can be observed in the forward geometry also by using x-polarized pump for instance). The medium interacts with two counter-propagating pumps $[(\omega_\ell, \vec{k}_\ell)$ and $(\omega_\ell, -\vec{k}_\ell)]$ with polarizations σ^+ and σ^- and a probe beam $[(\omega_s, \vec{k}_s)$ with polarization $\sigma^\pm]$ which is almost collinear with the σ^+ pump. The four-wave mixing process generates a conjugate wave $(2\omega_\ell - \omega_s, -\vec{k}_s)$ with polarization $\sigma^\mp$. The transient FWM signal $S_\pm(t)$ is proportional to $|P_\mp(t)|^2$, where $P_\pm(t)$ refers to $\vec{P}.\hat{\epsilon}^*_{\pm 1}$, and where

$$\hat{\epsilon}^*_{\pm 1} = \mp (\hat{x} \pm i\hat{y})/\sqrt{2} \qquad \hat{\epsilon}_0 = \hat{z} \tag{5.9}$$

are the basis vectors in the spherical representation. Note that in the spherical representation, one can express the third-order induced polarization, for instance, as

$$P^{(3)}_\mu(t) = \left(\frac{1}{2\pi}\right)^3 \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \; e^{-i(\omega_1+\omega_2+\omega_3)t}$$

$$\times (-1)^{\alpha+\beta+\gamma} \chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)E_{-\alpha}(\omega_1)E_{-\beta}(\omega_2)E_{-\gamma}(\omega_3) \quad , \qquad (5.10)$$

where now the tensorial indices μ,α,β,γ refer not to the cartesian indices $\hat{x}$, $\hat{y}$, $\hat{z}$ but to the spherical indices $\hat{e}_o,\hat{e}_{+1},\hat{e}_{-1}$ defined by (5.9). The structure (5.10) arises essentially from the fact that the interaction Hamiltonian in the spherical representation is written as

$$H_f(t) = -\vec{d}.\vec{E}$$

$$= -\sum_{\alpha}^{-} (-1)^{\alpha} d^{\alpha}E_{-\alpha} \qquad (5.11)$$

where α takes values 0, ±1 and d^{α}, E^{α} respectively refer to $\vec{d}.\hat{\epsilon}^{*}_{\alpha}$ and $\vec{E}.\hat{\epsilon}^{*}_{\alpha}$. The component $P_+(t)$ of the induced polarization $\vec{P}(t)$ can be expressed in terms of the transient FWM susceptibility as

$$P_+(t) \propto e^{-i(2\omega_\ell-\omega_s)t} \chi^{(3)}_{+-+-}(\omega_\ell,\omega_\ell,-\omega_s,t)\, e^{+}_{\ell}e^{-}_{\ell}(e^{+}_{s})^{*} + c.c. \qquad (5.12)$$

Here $\vec{e}_\ell$ and $\vec{e}_s$ respectively are the strengths of the pump and probe fields. The expression for $P_-(t)$ can be obtained from (5.12) by interchanging the plus and minus signs. The transient FWM susceptibility $\chi^{(3)}_{+-+-}(\omega_\ell,\omega_\ell,-\omega_s,t)$ can be obtained from the corresponding steady-state susceptibility by using the prescription (5.1)-(5.2). The steady-state susceptibility for the model system of Fig.3 is given by

$$\chi^{(3)}_{+-+-}(\omega_\ell,\omega_\ell,-\omega_s) = -\frac{N}{3!}\frac{d^-_{31}d^+_{13}d^+_{32}d^-_{23}}{(2\omega_\ell-\omega_s-\Lambda_{23})(\omega_\ell-\omega_s-\Lambda_{21})}\left[\frac{1}{\omega_\ell-\Lambda_{23}}\right.$$

$$\left.+\frac{1}{-\omega_s-\Lambda_{31}}\right]-\frac{d^+_{32}d^-_{23}}{2\omega_\ell-\omega_s-\Lambda_{23}}\times\left[d^-_{31}d^+_{13}\left(\frac{1}{\omega_\ell-\Lambda_{13}}+\frac{1}{-\omega_s-\Lambda_{31}}\right)\right.$$

$$\left.+2\,d^-_{23}d^+_{32}\left(\frac{1}{\omega_\ell-\Lambda_{23}}+\frac{1}{-\omega_s-\Lambda_{32}}\right)\right]$$

$$\times\frac{1}{\omega_\ell-\omega_s+i\gamma}\ . \qquad (5.13)$$

Note that the term $(\omega_\ell-\omega_s-\Lambda_{21})^{-1}$ with $\omega_\ell=\omega_s$ corresponds to the usual pressure-induced Hanle resonance[40,62] at $\omega_{12}=0$ [ω_{12} is proportional to the magnetic field], which survives only if $\Gamma^{ph}_{21}-\Gamma^{ph}_{23}-\Gamma^{ph}_{31}\neq 0$. However, even in the absence of collisions the transient FWM susceptibility will contain the resonance $[\omega_\ell-\omega_s-\omega_{21}+i(\Gamma_{23}-\Gamma_{13})]^{-1}$ which arises from a difference of the denominators underscored in the expression (5.13). Note that in the absence of collisions we have $\Gamma_{23}=\Gamma_{13}=\gamma/2$, $\Gamma_{12}=\gamma$. Thus the resonances at $\omega_\ell-\omega_s=\pm\omega_{12}$ that occur in the transient FWM susceptibility of the above three-level model system are of the same kind as the transient resonance at $\omega_\ell-\omega_s=0$ in the case of a two-level system discussed in Section A above. In the case when the fields are detuned far away from the optical transitions [i.e., in the limit $\Delta>>\gamma$], the transient FWM signal has a simple structure and is given by

$$S_\pm(t) = \left|\frac{2i\gamma t e^{i\Delta t-\gamma t/2}}{\Delta^2}\left[3e^{\pm i\delta t}\left(\frac{e^{i\Omega t}-1}{i\Omega t}\right)\right.\right.$$

$$+ \frac{e^{\mp i\delta t}(e^{i(\Omega\pm 2\delta)t}-1)}{i(\Omega\pm 2\delta)t} \Bigg] \Bigg|^2 , \quad \Omega = \omega_\ell - \omega_s , \qquad (5.14)$$

where 2δ is the energy separation between $|1\rangle$ and $|2\rangle$ and Δ is the atom-pump detuning in the absence of the magnetic field. The approximate expression (5.14) clearly shows the transient extra resonances at $\Omega=0, \pm 2\delta$. We have plotted in Fig.8 the complete expression for transient FWM signal $S_+(t)$ as a function of the magnetic field, (i.e., the energy separation between $|1\rangle$ and $|2\rangle$), in the case when all the fields have the same frequency. Our results clearly show the existence of the Hanle resonances in the transient signals. We set $\Omega=0$ for Fig.8 so that

$$S_\pm(t) \propto \frac{(\gamma t)^2 e^{-\gamma t}}{\Delta^4} \left[\frac{9}{16} + \frac{1}{16} \frac{\sin^2\delta t}{\delta^2 t^2} + \frac{3}{8} \frac{\sin 2\delta t}{2\delta t} \right] . \qquad (5.15)$$

The Hanle resonance corresponds to $\delta=0$. This transient Hanle resonance which is quite strong for $\gamma t \lesssim 1$, starts disappearing as t increases. However, it is restored back in the steady state if collisions are present. It is important to note that the transient signal, in contrast to the steady-state signal, is of the order of $1/\Delta^4$ rather than $1/\Delta^6$. Note that for $\gamma t=0.1$ the signal is narrower than for $\gamma t = 0.05$. With further increase in γt one expects much narrower signals. However, as argued in Section A, if the residual Doppler width is to remain much smaller than the observation-time width, then we have to work on a time-scale $\gamma t \ll 1$. Note also that for the values of γt that we have considered in Fig.8 [as also in

Fig.6] the signals grow with time. This is due to the fact that for short times, the t^2 term in (5.8) and (5.15) dominantes over the exponential term.

We have also examined the practical problem associated with the observation of the signal in the transient domain[62] and we find that the basic features of the extra resonances in the transient domain remain unchanged. For example we have averaged the signal over the detector response time

$$\langle S(t) \rangle = \frac{1}{t_d} \int_{t}^{t+t_d} d\tau \, S(\tau) \qquad (5.16)$$

We find that the signal in Figs.6,7 and 8 essentially remains unchanged for $\gamma t_d \sim 0.01$. For example we have compared in Fig.8 the averaged and the unaveraged signals in the case of transient Hanle resonance. We have also examined the effect of the switch-on of the various fields. For this purpose we have taken the field envelopes of the form $(1-e^{-\beta t})$. Thus β^{-1} gives the rise-time of the fields. The dashed curve in Fig.6 gives the transient signal for non-zero values of the rise-time. It is clear that the extra resonance in the transient domain survives though it gets a little bit distorted at the centre.

Thus, in conclusion, we have established on very general grounds the existence of new resonances in transient nonlinear spectroscopy. These resonances do not depend for their existence on the presence of atom-buffer gas collisions, source fluctuations or pump saturation. However these resonances do not survive in the long-time limit. The new resonances are characterized by linewidths determined essentially by the interaction time. In the context of transient four-wave mixing in model two and three-level systems, the various features of these resonances are studied.

CHAPTER VI

NONLINEAR RESPONSE IN PRESENCE OF CROSSRELAXATION

In Chapter II we had developed a nonlinear response theory that is valid under arbitrary relaxation conditions. In particular, working with a relaxation model which included the phase-changing as well as the inelastic collisions, we calculated explicit expressions for the nonlinear susceptibilities to various orders. We discussed various effects which arise due to the purely dephasing as well as the inelastic collisions. As is evident from (2.3), the above model consists basically of two types of relaxation parameters namely (i) γ_{ij}, the inelastic rates of transition from level $|j\rangle$ to $|i\rangle$ and (ii) Γ_{ij} [Eq.(2.4)], the rate of decay of the coherence ρ_{ij} between the levels $|i\rangle$ and $|j\rangle$. However, as is well-known, collisions not only give rise to a transfer of populations among the various energy levels and to a decay of coherence between the levels, but there can be an interference[65] too, between two collision-induced transitions. Such an interference becomes significant when the rate of the collision-induced transitions becomes appreciable compared to the frequency-separation between those transitions. Such interferences give rise to couplings between different coherences or between coherences and populations in the equations of motion for the density operator of the system. Hence in order to describe the nonlinear response of systems in which such interferences are important, the relaxation model must include these new coupling terms, apart from

the usual relaxation parameters γ_{ij} and Γ_{ij}. A simple case of such couplings, namely the coupling that gives rise to a transfer of coherence (or crossrelaxation) between two pairs of levels, has been discussed in some detail in the literature.[32,66,67] Crossrelaxation has been found to give rise to interesting effects in the linear response of a system to an external field, e.g., the collapse of the inversion spectrum of NH_3 at high pressures,[32] and the mixing of the two lines in the absorption spectrum, their merger into a single line and further, the narrowing of this line with increasing pressure.[66] The question of how crossrelaxation affects the nonlinear response[66-68] too is quite interesting. In this chapter, we examine the effect of crossrelaxation on the third-order nonlinear processes, namely saturated absorption and four-wave mixing. In Section III, we trace the origin of crossrelaxation to certain non-secular (or counter-rotating) terms in the master equation[69] describing the interaction of an atomic system with the bath of perturbers. In Section II, we specialize the general formulation of Section II to a model four-level system with two optical transitions. We study the effect of crossrelaxation on saturated abosrption. In Section IV, we calculate the nonlinear susceptibility for four-wave mixing in the model system of Section III. We present detailed numerical results for a range of collisional parameters.

II. ATOMIC DYNAMICS WITH CROSSRELAXATION

The relaxation behaviour of an atomic system in the presence of collisions can be handled by using various methods. For example, one can consider the interaction of an atom with a heat bath and write the interaction in the form

$$H = \sum_{m}^{-} E_m |m\rangle\langle m| + \sum_{k\ell}^{-} v_{k\ell} |k\rangle\langle \ell| + H_R \quad , \tag{6.1}$$

where v describes the interaction of the atom with the heat bath or with the perturbers and H_R is the unperturbed Hamiltonian of the heat bath. Note that v_{kl} is an operator in the Hilbert space of the perturbers. Let ρ be the reduced density matrix for the multilevel atom of interest. In the weak coupling limit and in the Markov (impact) approximation, the density matrix ρ^I in the interaction picture is found to obey the equation[69]

$$\frac{\partial}{\partial t}\rho^I = \sum_{k\ell mn}^{-} \Big\{ \big(A_{mn}\rho^I A_{k\ell} - A_{kn}\rho^I \delta_{\ell m} \big) \gamma^{+}_{k\ell mn} + \big(A_{k\ell}\rho^I A_{mn} - \rho^I A_{m\ell}\delta_{nk} \big) \gamma^{-}_{mnk\ell} \Big\} e^{i(\omega_{k\ell}+\omega_{mn})t} \quad , \tag{6.2}$$

where

$$A_{k\ell} = |k\rangle\langle \ell| \quad , \quad \omega_{k\ell} = E_k - E_\ell \quad , \tag{6.3}$$

and the coefficients $\gamma^{\pm}$ are related to the correlation functions of the perturber bath

$$\gamma^{+}_{k\ell mn} = \int_0^\infty d\tau \, \langle v_{k\ell}(\tau) \, v_{mn}(0) \rangle \, e^{-i\omega_{mn}\tau} \quad , \tag{6.4}$$

$$\gamma^{-}_{k\ell mn} = \int_0^\infty d\tau \, \langle v_{mn}(0) \, v_{k\ell}(\tau) \rangle \, e^{-i\omega_{mn}\tau}$$

$$= (\gamma^{+}_{\ell knm})^{*} \tag{6.5}$$

At this point one usually makes the rotating – wave approximation and keeps only those terms in Eq.(6.2) for which $\omega_{k\ell}+\omega_{mn}$ is exactly equal to zero. Then, in the case when the atom has a non-equidistant and non-degenerate spectrum, one gets the well-known equation which has been extensively used in finding the nonlinear response of a driven system:

$$\frac{\partial}{\partial t} \rho^{I}_{ij} = -\Gamma_{ij}(1-\delta_{ij}) \, \rho^{I}_{ij} + \delta_{ij} \sum_{k\neq 1}^{-} (\gamma_{ik}\rho^{I}_{kk} - \gamma_{ki}\rho^{I}_{ii}) \quad , \tag{6.6}$$

where

$$\Gamma_{ij} = 1/2 \sum_{k}^{-} (\gamma_{ki} + \gamma_{kj}) + \Gamma^{ph}_{ij} \quad . \tag{6.7}$$

Here γ_{ij} is the rate of transition from $|j\rangle$ to $|i\rangle$ due to spontaneous emission as well as due to inelastic collisions, and Γ^{ph}_{ij} the rate of dephasing due to elastic collisions. However, the counter-rotating terms in Eq.(6.2) can be important in certain cases as discussed below. When counter-rotating terms are retained, then Eq.(6.2) can be written in the Schroedinger picture as

$$\frac{\partial}{\partial t}\rho_{ij} = -i\Lambda_{ij}\rho_{ij} + \sum_{nk}\xi_{kjin}\rho_{nk} - \sum_{k}(\eta^{+}_{ik}\rho_{kj} + \eta^{-}_{kj}\rho_{ik}) \quad , \ (i \neq j),$$

(6.8)

$$\frac{\partial}{\partial t}\rho_{ii} = \sum_{k\neq i}(\gamma_{ik}\rho_{kk} - \gamma_{ki}\rho_{ii}) + \sum_{nk}(1-\delta_{nk})\xi_{kiin}\rho_{nk}$$

$$- \sum_{k}(\eta^{+}_{ik}\rho_{ki} + \eta^{-}_{ki}\rho_{ik}) \quad , \tag{6.9}$$

where

$$\xi_{kjin} = \gamma^{+}_{kjin} + \gamma^{-}_{kjin} \quad ,$$

$$\eta^{+(-)}_{ij} = (1-\delta_{ij})\sum_{k}\gamma^{+(-)}_{ikkj} \quad ,$$

$$\Lambda_{ij} = \omega_{ij} - i\Gamma_{ij} \quad . \tag{6.10}$$

In Eqs.(6.8) and (6.9), the ξ and η terms are the counter-rotating terms that bring about coherence-coherence and coherence-population coupling. Let us now look at the origin and meaning of such additional terms. Expressing Eq.(6.4) in a representation in which the bath Hamiltonian is diagonal, i.e., $H_R|R\rangle = R|R\rangle$, we get[70]

$$\gamma^{+}_{klmn} = \pi\sum_{R} f_o(R) \langle R, k|V|R-\omega_{mn}, \ell\rangle\langle R,n|V|R-\omega_{mn}, m\rangle^{*} \quad ,$$

(6.11)

and we also have

$$\gamma_{\ell k} = \gamma^{+}_{k\ell\ell k} + \gamma^{-}_{k\ell\ell k} = 2\pi \sum_{R} f_o(R) |\langle R,k|V|R-\omega_{\ell k}, \ell\rangle|^2 \quad , \qquad (6.12)$$

where $f_o(R)$ is the probability distribution of the bath states. One can see from Eqs.(6.11) and (6.12), that while $\gamma^{+}_{k\ell mn}$ is related to a product of two transition amplitudes of the form $c_{\ell k}c^{*}_{mn}$ (where c_{ij} denotes the probability amplitude that a transition takes place from $|j\rangle$ to $|i\rangle$), $\gamma_{\ell k}$ is related to the modulus-squared of the transition amplitude of the form $|c_{\ell k}|^2$ Thus the terms $\gamma^{+}_{k\ell mn}$ can be seen to arise from a quantum-mechanical interference between the two transitions $|k\rangle \rightarrow |\ell\rangle$ and $|n\rangle \rightarrow |m\rangle$. One can take the magnitude of $\gamma^{+(-)}_{k\ell mn}$ to be roughly equal to $\sqrt{(\gamma_{\ell k}\gamma_{mn})}/2$. By doing a simple first-order perturbation theory with any particular counter-rotating term as the perturbation parameter, one can estimate the order of its contribution to $\rho(t)$. For instance, the contribution from the term ξ_{kjin} that couples the coherences ρ_{ij} and ρ_{nk} can be seen to important when $\xi_{kjin}[\sim\sqrt{(\gamma_{jk}\gamma_{in})}]$ is appreciable compared to $|\Lambda_{ij}-\Lambda_{nk}|$. There are many systems for which some of the non-secular couplings become important (at high pressures) when the inelastic collision rates become sufficiently large. In the next section, we study a model system where a simple coherence-coherence coupling between two pairs of levels is important. Such a model system has been of considerable interest. Other systems can also be studied similarly.

III. EFFECT OF CROSSRELAXATION ON THIRD-ORDER NONLINEAR SUSCEPTIBILITIES

Consider a frequently[65-67] studied four-level system consisting of two transitions $|1\rangle \leftrightarrow |2\rangle$ and $|3\rangle \leftrightarrow |4\rangle$ coupled by inelastic collisions (see Fig. 4) and interacting with external fields. A central frequency ω_o is defined so that $\omega_{12}=\omega_o-\delta$, $\omega_{34}=\omega_o+\delta$. The time evolution of the system is described by the equation

$$\frac{\partial \rho}{\partial t} = L_o\rho + L_f(t)\rho \quad , \tag{6.13}$$

where $L_o\rho$ is as given by (6.8),(6.9) and $L_f(t)$ is the Liouville operator describing atom-field interaction. For the above system, the relaxation part $L_o\rho$ of (6.13) is given by

$$\begin{bmatrix} (L_o\rho)_{12} \\ (L_o\rho)_{34} \end{bmatrix} = M \begin{bmatrix} \rho_{12} \\ \rho_{34} \end{bmatrix}, \quad \begin{bmatrix} (L_o\rho)_{21} \\ (L_o\rho)_{43} \end{bmatrix} = M^* \begin{bmatrix} \rho_{21} \\ \rho_{43} \end{bmatrix}, \tag{6.14}$$

$$M = \begin{bmatrix} -i\Lambda_{12} & \xi \\ \xi & -i\Lambda_{34} \end{bmatrix} ,$$

$$\Lambda_{12}= \omega_o - \delta - i(\gamma + \sigma) , \quad \Lambda_{34} = \omega_o + \delta - i(\gamma + \sigma) , \tag{6.15}$$

and

$$\begin{bmatrix} (L_o\rho)_{11} \\ (L_o\rho)_{22} \\ (L_o\rho)_{33} \\ (L_o\rho)_{44} \end{bmatrix} = \begin{bmatrix} -(2\gamma+\sigma) & 0 & \sigma & 0 \\ 2\gamma & -\sigma & 0 & \sigma \\ \sigma & 0 & -(2\gamma+\sigma) & 0 \\ 0 & \sigma & 2\gamma & -\sigma \end{bmatrix} \begin{bmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{bmatrix} \tag{6.16}$$

Here we have taken $\xi_{2431}=\xi_{4213}=\xi_{3124}=\xi_{1342} = \xi$ (all other ξ and η terms are negligible), $\Gamma_{12}=\Gamma_{34}=\gamma+\sigma$, $\Gamma^{ph}=0$. σ is thus the rate of the inelastic collisions between two nearby levels as shown in Fig.4. The parameter ξ couples coherences to coherences. These parameters σ and ξ can be obtained in terms of the matrix elements of V [see Eq.(6.11)]. These can also be related[65] to the collision matrix S, e.g., $\xi = \int (S^+)_{31} S_{24} F(g) dg$, where F(g) can, for example, be the distribution of impact parameters g. For the calculation of the nonlinear susceptibilities (2.30) for this model, it is necessary to know the eigenvalues and eigenfunctions of L_o. Note that since there is a coupling between ρ_{12} and ρ_{34}, Eq.(2.5) does not hold. Hence L_o is no longer diagonal in the Liouville sub-space of vectors $|i\rangle\langle j|$ $(i\neq j)$. Thus one needs to solve an eigenvalue problem as illustrated in (2.7),(2.8), in the $|i\rangle\langle j|$ $(i\neq j)$ basis too. For the $[|1\rangle\langle 2|, |3\rangle\langle 4|]$ basis, for instance, the eigenvalue problem can be written as

$$L_o\phi_i = \kappa_i\phi_i \quad ,$$

$$\phi_i = U_{1i}|1\rangle\langle 2| + U_{2i}|3\rangle\langle 4|,$$

$$|1\rangle\langle 2| = \sum_i U^{-1}_{i1}\,\phi_i \quad , \quad |3\rangle\langle 4| = \sum_i U^{-1}_{i2}\,\phi_i \quad , \quad i=1,2, \qquad (6.17)$$

where U is the matrix which diagonalizes M, i.e.,

$$U^{-1}MU = \begin{pmatrix} \kappa_1 & 0 \\ 0 & \kappa_2 \end{pmatrix} \quad . \qquad (6.18)$$

We have shown that

$$\kappa_{1,2} = -\frac{i}{2}\left[\Lambda_{12}+\Lambda_{34}\right] \pm \sqrt{(\xi^2-\beta^2)} \ ,$$

$$U_{11} = U_{22} = 1 \ , \ U_{12} = -U_{21} = -\frac{\xi}{(i\beta+\sqrt{(\xi^2-\beta^2)})} \ ,$$

$$\beta = \frac{1}{2}\left[\Lambda_{12}-\Lambda_{34}\right] \quad . \qquad (6.19)$$

Note that since the relaxation matrix corresponding to the $[|2\rangle\langle 1|, |4\rangle\langle 3|]$ basis is M^*, the eigenvalues and eigenfunctions in this basis are κ_1^*, κ_2^* and ϕ_1^+, ϕ_2^+ respectively. Thus using (6.17) and (2.7),(2.8) one can obtain the action of an arbitrary function $f(L_o)$ of L_o on an arbitrary operator Q. We expand $(\omega - iL_o)^{-1}\,|i\rangle\langle j|$ in terms of the complete set of operators $|k\rangle\langle \ell|$ and write

$$(\omega - iL_o)^{-1}\,|i\rangle\langle j| = \sum_{k\ell} D_{ijk\ell}(\omega)\,|k\rangle\langle \ell| \quad . \qquad (6.20)$$

For the present model (6.16), there is no coherence-population coupling and hence

$$D_{iikk}(\omega) = B_{ik}(\omega) \quad , \qquad (6.21)$$

where $B_{lk}(\omega)$ is defined by Eq.(2.34) with the relaxation matrix now given by (6.16). For the above model, we have shown using (6.17)-(6.19) that

$$D_{1212}(\omega) = \frac{a_-}{\omega - i\kappa_1} + \frac{a_+}{\omega - i\kappa_2} \quad ,$$

$$D_{1234}(\omega) = D_{3412}(\omega) = b\left(\frac{1}{\omega - i\kappa_1} - \frac{1}{\omega - i\kappa_2} \right) \quad ,$$

$$D_{3434}(\omega) = \frac{a_+}{\omega - i\kappa_1} + \frac{a_-}{\omega - i\kappa_2} \quad ,$$

$$a_\pm = \frac{1}{2}\left(1 \pm \frac{i\beta}{\sqrt{(\xi^2 - \beta^2)}} \right) \quad , \quad b = \frac{\xi}{2\sqrt{(\xi^2 - \beta^2)}} \quad . \qquad (6.22)$$

Note that $D_{2121}(\omega)$, $D_{2143}(\omega)$, $D_{4321}(\omega)$ and $D_{4343}(\omega)$ can be simply obtained by replacing $a_\pm$, b and $\kappa_{1,2}$ by their complex conjugates in the expressions for $D_{1212}(\omega)$, $D_{1234}(\omega)$, $D_{3412}(\omega)$ and $D_{3434}(\omega)$ respectively. The quantities $B_{ij}(\omega)$ can be worked out using (2.34) in terms of the elements of the population relaxation matrix R defined by Eq.(6.16). We have shown that

$$B_{11}(\omega) = B_{33}(\omega) = \frac{1}{2(\omega + 2i\gamma)} + \frac{1}{2(\omega + 2i(\gamma+\sigma))}$$

$$B_{13}(\omega) = B_{31}(\omega) = \frac{1}{2(\omega + 2i\gamma)} - \frac{1}{2(\omega + 2i(\gamma+\sigma))}$$

$$B_{22}(\omega) = B_{44}(\omega) = \frac{1}{2(\omega + 2i\sigma)} + \frac{1}{2\omega}$$

$$B_{24}(\omega) = B_{42}(\omega) = -\frac{1}{2(\omega + 2i\sigma)} + \frac{1}{2\omega}$$

$$B_{12}(\omega) = B_{34}(\omega) = B_{22}(\omega) - B_{11}(\omega)$$

$$B_{14}(\omega) = B_{32}(\omega) = B_{24}(\omega) - B_{13}(\omega) \quad . \tag{6.23}$$

Having obtained the relevant propagators $D_{ijk\ell}(\omega)$ for the above model, the calculation of the nonlinear susceptibilities (2.30) to various orders is now straightforward. Let the system be interacting with two similarly polarized monochromatic fields with frequencies ω_s and ω_ℓ. We write the total field as

$$\vec{E}(t) = \vec{E}_s(t) + \vec{E}_\ell(t) \quad ,$$

$$\vec{E}_s(t) = \hat{e}(e_s e^{-i\omega_s t} + c.c.) \quad ,$$

$$\vec{E}_\ell(t) = \hat{e}(e_\ell e^{-i\omega_\ell t} + c.c.) \quad . \tag{6.24}$$

We will now obtain the results for the nonlinear response of the system when crossrelaxation is important.

A. Linear Response

The general expression for the first-order susceptibility can be obtained from (2.30) in terms of the $D_{ijk\ell}$ defined in (6.20). From (2.30) we have

$$\chi^{(1)}_{\mu\alpha}(\omega) = i N \mathrm{Tr}\left\{ d^\mu (\omega - iL_o)^{-1} L_\alpha \rho^{(o)} \right\} \quad . \tag{6.25}$$

On writing

$$\rho^{(o)} = \sum_{i}^{-} \rho_{ii}^{(o)} |i\rangle\langle i| \qquad (6.26)$$

and using the definition of L_α[Eq.(2.30)],Eq.(6.25) can be reduced to

$$\chi_{\mu\alpha}^{(1)}(\omega) = - N \sum_{ik}^{-} d_{ki}^{\alpha} (\rho_{ii}^{(o)} - \rho_{kk}^{(o)}) \, Tr\{ d^{\mu} (\omega - iL_o)^{-1} |k\rangle\langle i| \} \, , \qquad (6.27)$$

Equation (6.27) can be simplified by using (6.20). Thus we have

$$\chi_{\mu\alpha}^{(1)}(\omega) = - N \sum_{ik\ell m}^{-} \left(\rho_{ii}^{(o)} - \rho_{kk}^{(o)} \right) d_{\ell m}^{\mu} \, d_{ki}^{\alpha} \, D_{kim\ell}(\omega) \, . \qquad (6.28)$$

For the model system of Fig.4, $\rho_{22}^{(o)} = \rho_{44}^{(o)} = \frac{1}{2}$ and hence (6.25) becomes

$$\chi_{\mu\alpha}^{(1)}(\omega) = - \frac{N}{2} \{ d_{21}^{\mu} [d_{12}^{\alpha} D_{1212}(\omega) + d_{34}^{\alpha} D_{1234}(\omega)]$$

$$+ d_{43}^{\mu} [d_{12}^{\alpha} D_{3412}(\omega) + d_{34}^{\alpha} D_{3434}(\omega)]$$

$$+ |1\rangle \leftrightarrow |2|\rangle \, , \quad |3\rangle \leftrightarrow |4\rangle \} \, . \qquad (6.29)$$

Consider all fields to be similarly polarized and let $d_{12} = d_{34} = d$ (real). The energy absorbed by the system from the probe field is given by

$$I = \left\langle \frac{\partial \vec{P}(t)}{\partial t} \cdot \vec{E}_s(t) \right\rangle \qquad (6.30)$$

where $\vec{P}(t)$ is the induced polarization which we write as

$$\vec{P}(t) = \vec{p}(\omega_s)\, e^{-i\omega_s t} + c.c. \qquad (6.31)$$

The brackets $\langle \ldots \rangle$ in (6.30) refer to time-averaging. It follows from (6.30) and (6.31) that

$$I = 2\omega_s \, \mathrm{Im} \left[\vec{p}(\omega_s) . \hat{e}\, e_s^* \right] \qquad (6.32)$$

In the absence of the pump field ω_ℓ, the linear absorption is given by

$$I_1(\omega_s) = 2\omega_s \, \mathrm{Im} \left[\vec{p}^{(1)}(\omega_s) \cdot \hat{e}\, e_s^* \right]$$

$$= 2\omega_s \, |e_s|^2 \, \mathrm{Im} \left[\chi^{(1)}(\omega_s) \right] \quad . \qquad (6.33)$$

It follows from (6.29) that

$$\chi^{(1)}(\omega_s) = - \frac{N d^2}{2} \left(\frac{A_+}{\Delta_s - i\lambda_+} + \frac{A_-}{\Delta_s - i\lambda_-} \right) \qquad (6.34)$$

where

$$\Delta_s = \omega_s - \omega_o$$

$$\lambda_\pm = - (\gamma + \sigma) \pm \sqrt{(\xi^2 - \delta^2)}$$

$$A_{\pm} = a_{+} + a_{-} \pm 2b = 1 \pm \frac{\xi}{\sqrt{(\xi^2-\delta^2)}} \quad . \qquad (6.35)$$

Note that in deducing (6.34), we have thrown away the non-rotating terms that are contained in $|1\rangle \leftrightarrow |2\rangle$, $|3\rangle \leftrightarrow |4\rangle$ in (6.29). The behaviour of $\chi^{(1)}$ depends on the magnitude of crossrelaxation. For $\xi/\delta < 1$, one has

$$\text{Im } \chi^{(1)}(\omega_s) \propto \frac{\gamma+\sigma+\alpha\,[\Delta_s + \sqrt{(\delta^2-\xi^2)}]}{[\Delta_s+\sqrt{(\delta^2-\xi^2)}]^2 + (\gamma+\sigma)^2} + \frac{\gamma+\sigma-\alpha[\Delta_s - \sqrt{(\delta^2-\xi^2)}]}{[\Delta_s-\sqrt{(\delta^2-\xi^2)}]^2 + (\gamma+\sigma)^2} \,,$$

$$\alpha = \frac{\xi}{\sqrt{(\delta^2-\xi^2)}} \quad . \qquad (6.36)$$

One can see from Eq.(6.36) that for $\xi/\delta < 1$, the linear absorption spectrum consists of two lines exhibiting both absorptive and dispersive character. These lines get more and more mixed as σ increases (static mixing) and as ξ increases (dynamic mixing). In the limit $\xi/\delta \to 0$, Eq.(6.36) reduces to a sum of two Lorentzians

$$\text{Im } \chi^{(1)}(\omega_s) \propto \frac{\gamma+\sigma}{(\Delta_s+\delta)^2+(\gamma+\sigma)^2} + \frac{\gamma+\sigma}{(\Delta_s-\delta)^2+(\gamma+\sigma)^2} \quad . \qquad (6.37)$$

At $\xi/\delta = 1$, one has a single line peaked at $\Delta_s=0$ and with width $\gamma+\sigma$. In general, the first-order spectrum is symmetrical around $\Delta_s=0$. For $\xi/\delta > 1$, one has

$$\text{Im } \chi^{(1)}(\omega_s) \propto \left[\frac{A_{+}\lambda_{+}}{\Delta_s^2 + \lambda_{+}^2} + \frac{A_{-}\lambda_{-}}{\Delta_s^2 + \lambda_{-}^2} \right] \,, \qquad (6.38)$$

where the $A_{\pm}$, $\lambda_{\pm}$ are as given in (6.35). Thus, as ξ/δ increases beyond 1, one of the two lines becomes narrower and stronger while the other line becomes broader and weaker and what survives is the narrower line. For $\xi/\delta \sim \sigma/\delta >> 1$, one has

$$\lambda_+ \sim -\gamma - \delta^2/2\sigma \quad , \quad A_+ \sim 2 + \delta^2/2\sigma \quad ,$$

$$\lambda_- \sim -(\gamma + 2\sigma) + \delta^2/2\sigma \quad , \quad A_- \sim -\delta^2/2\sigma \qquad (6.39)$$

Hence, at very high pressures, one observes a single narrow line with width approaching natural linewidth. This is the well-known line narrowing phenomena[65-67] resulting from the mixing of the lines.

B. Susceptibility for saturated absorption with crossrelaxation

We next consider absorption from a probe in presence of a pump field. The absorption spectrum in such a case is given by

$$I_3(\omega_s) = 2\omega_s |e_s|^2 \, \mathrm{Im}\, [\chi^{(1)}(\omega_s) + |e_\ell|^2 \chi^{(3)}(\omega_\ell, -\omega_\ell, \omega_s)] \, , \qquad (6.40)$$

where $\chi^{(1)}(\omega_s)$ is as given by Eq.(6.34) and the quantity $\chi^{(3)}(\omega_\ell, -\omega_\ell, \omega_s)$ is 6 times the susceptibility $\chi^{(3)}(\omega_\ell, -\omega_\ell, \omega_s)$. Note that using (6.20) in (2.30), we can write down a general expression for the third-order susceptibility which is valid in presence of crossrelaxation. We have shown that

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3) = \frac{N\_sym}{31} \sum_{ik,j\ell mnpqrs} \left(\rho^{(o)}_{ii} - \rho^{(o)}_{kk} \right) d^{\gamma}_{ik} D_{ikj\ell}(\omega_3)$$

$$\times \left(d^{\beta}_{mj} D_{m\ell np}(\omega_2,\omega_3) - d^{\beta}_{\ell m} D_{jmnp}(\omega_2,\omega_3) \right)$$

$$\times \left(d^{\alpha}_{qn} D_{qprs}(\omega_p) - d^{\alpha}_{pq} D_{nqrs}(\omega_p) \right) d^{\mu}_{sr} \quad ,$$

$$\omega_p = \omega_1 + \omega_2 + \omega_3 \quad , \qquad (6.41)$$

where the symbol 'sym' has the usual meaning as in (2.30), that the sum on the right hand side has to be symmetrized with respect to the indices (ω_1,α), (ω_2,β) and (ω_3,γ). Note that we will obtain the usual expression for the third-order susceptibility (2.30) by substituting in (6.41), the relation

$$D_{ijk\ell}(\omega) = \delta_{ik}\delta_{j\ell}(\omega-\Lambda_{ij})^{-1} + \delta_{ij}\delta_{k\ell}C_{ik}(\omega) \qquad (6.42)$$

The relation (6.42) is valid when all non-secular couplings are neglected. For the model system of Fig. 4, we can calculate $\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s)$ using the general expression (6.41) and the relations (6.22), (6.23). We have shown that

$$\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s) = \frac{1}{6}\left[Nd^4/2 \right] \left\{ \left[\frac{}{\Delta_s - i\lambda_+} \quad \frac{A_-}{} \right] \right.$$

$$\left. \times \left[\frac{1}{\Delta_\ell + i\lambda_+} \left(\frac{1}{\Delta_s - i\lambda_-} + \frac{1}{\Delta_\ell - i\lambda_-} \right) + \frac{1}{\Delta_\ell + i\lambda_-} \left(\frac{1}{\Delta_s - i\lambda_+} + \frac{}{\Delta_\ell - i\lambda_+} \right) \right] \right.$$

$$- \frac{1}{\Delta_\ell + i\lambda_-} \left[\frac{1}{\Delta_s - i\lambda_+} + \frac{1}{\Delta_\ell - i\lambda_+} \right] \Bigg] + \left[\frac{A_+}{\Delta_s - i\lambda_+} + \frac{A_-}{\Delta_s - i\lambda_-} \right)$$

$$\times \left[\frac{g_1(\xi)}{\Delta_s - \Delta_\ell + 2i\gamma} + \frac{g_0(\xi)}{2i\gamma} \right] \Bigg\} \int , \qquad (6.43)$$

where

$$g_1(\xi) = \frac{4i(\sigma+\xi)[(\gamma+\sigma)^2 - \xi^2 + \delta^2 - i(\gamma+\sigma)(\Delta_s - \Delta_\ell)] + 2i[2\Delta_\ell \Delta_s \sigma - \xi(\Delta_s^2 + \Delta_\ell^2)]}{(\Delta_\ell + i\lambda_+)(\Delta_s - i\lambda_-)(\Delta_\ell + i\lambda_-)(\Delta_s - i\lambda_+)} , \qquad (6.44)$$

$$g_0(\xi) = g_1(\xi) \Big|_{\Delta_s = \Delta_\ell} \qquad (6.45)$$

Here the $A_\pm$ and $\lambda_\pm$ are as defined in (6.35), and $\Delta_\ell = \omega_\ell - \omega_0$. Note that we have dropped the tensor indices of $\chi^{(3)}$ in (6.43) since we considered all fields to be similarly polarized. Further note that the expression for $\chi^{(3)}$ in (6.43) does not have the usual permutation symmetry with respect to the frequencies $\omega_\ell, -\omega_\ell, \omega_s$ since in writing (6.43) we have thrown away the non-rotating (anti-resonant) terms. The non-rotating terms correspond to contributions from some of the permutations of $\omega_\ell, -\omega_\ell, \omega_s$. It is found that $\mathrm{Im}\chi^{(3)}(\omega_\ell, -\omega_\ell, \omega_s)$ can be negative. This can be seen by considering a special case of Eq.(6.43) with $\xi = \sigma = 0$. In this limit, we have

$$\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s) = \frac{1}{6}\left(\frac{Nd^4}{2}\right)\left[\frac{2}{(\Delta_s+\delta+i\gamma)(\Delta_\ell+\delta-i\gamma)}\left(\frac{1}{\Delta_s+\delta+i\gamma}\right.\right.$$

$$\left.\left.+\frac{1}{\Delta_\ell+\delta+i\gamma}\right)+\delta\rightarrow-\delta\right] \quad . \qquad (6.46)$$

Note that $\delta\rightarrow-\delta$ represents the same terms with δ interchanged with $-\delta$. The susceptibility (6.46) is just the sum of $\chi^{(3)}$'s for two independent two-level systems with resonance frequencies $\omega_o-\delta$ and $\omega_o+\delta$. Eq.(6.46) leads to

$$\text{Im}\,\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s) = -\frac{1}{6}\left(\frac{Nd^4}{2}\right)\left[\frac{4\gamma(\gamma^2+\Delta_{1\ell}\Delta_{1s})}{(\Delta_{1s}^2+\gamma^2)(\Delta_{1\ell}^2+\gamma^2)}+\text{terms with } 1\rightarrow2\right],$$

$$\Delta_{1\ell,1s} = \omega_o+\delta-\omega_{\ell,s}\ ,\quad \Delta_{2\ell,2s} = \omega_o-\delta-\omega_{\ell,s}\ . \qquad (6.47)$$

One can see from Eq.(6.47) that for $\Delta_{1\ell}=0$, for instance, $\text{Im}\chi^{(3)}$ remains negative for all values of Δ_{1s} for which it is significant. Hence it turns out that the third-order process gives rise to the possibility of amplificatipn[71] of the probe wave. However, the total absorption (6.40) will still be positive since the contribution of $\chi^{(3)}$ terms is small. This is seen from Fig.9. The amplification can be apparent, for example, by examining the absorption at two different values of the pump intensity. Further, one can see from Eq.(6.43) that $\chi^{(3)}$ has resonances at

$$\Delta_s = \Delta_\ell\ ,\ \pm\sqrt{(\delta^2-\xi^2)}\ , \qquad (6.48)$$

which should be well resolved if Δ_ℓ is large and if $\delta >> \xi$. Note that the resonance $\Delta_s=\Delta_\ell$ in the last term in (6.43) is the

pressure-induced extra resonance[5-7] which has been discussed extensively in the context of four-wave mixing. Figure 9 shows the resonances at $\Delta_s = \pm \sqrt{(\delta^2-\xi^2)}$. The resonance at $\Delta_s=\Delta_\ell$ is rather weak and gets washed away by the line mixing effects. This can be seen from the structure of the coefficient of the pressure-induced term in (6.40), namely $g_1(\xi)$ [Eq.(6.44)]. Note that in the numerator of the expression for $g_1(\xi)$, the quantities proportional σ and ξ occur with opposite signs. In particular for large detunings, i.e., $\Delta_s \sim \Delta_\ell = \Delta >> \gamma, \sigma, \xi$, we have $g_1(\xi) \sim 4i(\sigma-\xi)/\Delta^2$ so that the pressure-induced extra resonance at $\Delta_s=\Delta_\ell$ disappears if $\sigma=\xi$, and this is the case in Fig.9. We have checked numerically the existence of the PIER for $\xi=\sigma/2$ etc. Thus the effect of cross-relaxation ξ is to decrease the weight of the pressure-induced (σ-induced) component in the saturated absorption spectrum. We also observe a small asymmetry between the two resonances at $\Delta_s = \pm\sqrt{(\delta^2-\xi^2)}$, which is induced by the pump. Note also that the character of the resonance changes if Δ_ℓ (say) is chosen close to $\sqrt{(\delta^2-\xi^2)}$. Some of the resonances take the form of the square of a Lorentzian. The behavior of the absorption spectrum when the pump is tuned to one of the atomic transitions is shown in Fig.10. This tuning results in a smaller absorption. For $\xi/\delta=1$, Eq.(6.43) reduces to

$$\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s) = -\frac{1}{6}\left(\frac{Nd}{2}\right)^4\left\{\frac{2}{(2i\gamma+\Delta_s-\Delta_\ell)(\Delta_s+i(\gamma+\sigma))}\left[\frac{1}{\Delta_s+i(\gamma+\sigma)}\right.\right.$$

$$\left.\left. - \frac{1}{\Delta_\ell-i(\gamma+\sigma)}\right] + \frac{2}{2i\gamma(\Delta_s+i(\gamma+\sigma))}\left[\frac{1}{\Delta_\ell+i(\gamma+\sigma)} - \frac{1}{\Delta_\ell-i(\gamma+\sigma)}\right]\right\}, \tag{6.49}$$

which has the same structure as that of $\chi^{(3)}$ for a two-level system with transverse relaxation time $T_2=(\gamma+\sigma)^{-1}$ and longitudinal relaxation time $T_1=(2\gamma)^{-1}$. For $\xi/\delta \sim \sigma/\delta >> 1$,

$$\chi^{(3)}(\omega_\ell,-\omega_\ell,\omega_s) = \frac{1}{6}\left(\frac{Nd}{2}\right)^4\left\{\frac{2}{(\Delta_s+i\gamma)(\Delta_\ell-i\gamma)}\left[\frac{1}{\Delta_s+i\gamma}+\frac{1}{\Delta_\ell+i\gamma}\right]\right\} \tag{6.50}$$

resembles the $\chi^{(3)}$ for a two-level system when only radiative relaxation is present. Hence for $\xi/\delta > 1$, the saturated absorption spectrum will consist of a single narrow symmetrical line at $\Delta_s=0$, in much the same way as in the first-order spectrum, except for a slight reduction in the peak height depending on pump detuning and pump strength.

IV. NONLINEAR SUSCEPTIBILITY FOR FOUR-WAVE MIXING WITH CROSSRELAXATION

We next examine in detail the nonlinear susceptibility $\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s)$ describing four-wave mixing (FWM). For the model of Fig.4, we have shown using (6.22), (6.23) in (6.28) that

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s) = -\frac{1}{6}\left(\frac{Nd}{2}\right)^4\left[\frac{A_+}{\Omega-\Delta_\ell+i\lambda_+}+\frac{A_-}{\Omega-\Delta_\ell+i\lambda_-}\right]$$

$$\left[\frac{1}{(\Omega+\Delta_\ell+i\lambda_+)(\Delta_\ell-i\lambda_-)}+\frac{1}{(\Omega+\Delta_\ell+i\lambda_-)(\Delta_\ell-i\lambda_+)}\right]-A_+A_-\left[\frac{1}{\Omega-\Delta_\ell+i\lambda_+}\right.$$

$$\left.-\frac{1}{\Omega-\Delta_\ell+i\lambda_-}\right]\left[\frac{1}{(\Omega+\Delta_\ell+i\lambda_+)(\Delta_\ell-i\lambda_-)}-\frac{1}{(\Omega+\Delta_\ell+i\lambda_-)(\Delta_\ell-i\lambda_+)}\right]$$

where $\Omega=\omega_s-\omega_\ell$, $\Delta_\ell=\omega_\ell-\omega_o$ and $A_\pm,\lambda_\pm$ are defined by Eq.(6.35). Note again that in writing $\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s)$ in (6.50) we have dropped the tensor indices since all fields are similarly polarized. Further the expression in (6.50) does not exhibit the permutation symmetry with respect to the indices ω_ℓ,ω_ℓ and ω_s, because we have thrown away the non-rotating terms. Such non-rotating terms correspond to contributions from two of the permutations of ω_ℓ,ω_ℓ, and $-\omega_s$. Since the physically observable quantity is the induced polarization (the FWM signal is related to $|\vec{P}^{(3)}(t)|^2$) and not the susceptibility as such, a lack of permutation symmetry in the expression for $\chi^{(3)}$ [when rotating-wave approximation is made] will not lead to any physical consequences. The quantity $g_2(\xi)$ in (6.51) is obtained by interchanging Δ_s and Δ_ℓ in the expression for $g_1(\xi)$ in Eq.(6.44). One can see from Eq.(6.51) that for $\xi/\delta<1$, the resonances in $\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s)$ are at

$$\Omega = \Delta_\ell-\sqrt{(\delta^2-\xi^2)},\quad \Delta_\ell+\sqrt{(\delta^2-\xi^2)},\quad 0\ ,\ -[\Delta_\ell+\sqrt{(\delta^2-\xi^2)}],$$

$$-[\Delta_\ell-\sqrt{(\delta^2-\xi^2)}]\ . \qquad (6.52)$$

Thus depending on the magnitude of $\Delta_\ell \pm \sqrt{(\delta^2-\xi^2)}$, some of the lines may overlap. The width of the resonance at $\Omega=0$ is 2γ while the width of each of the other resonances is $\gamma+\sigma$. Consider the case when Δ_ℓ is negative and $\Delta_\ell+\sqrt{(\delta^2-\xi^2)}$ is far from zero. In such a case, all the five lines corresponding to the resonances in (6.51) are distinctly present. It can be seen from (6.52) that the lines corresponding to the first (third) and the second (fourth) reso-

nances dynamically mix with each other as ξ/δ increases. As in the linear absorption spectrum, here too the dynamic mixing is due to the fact that the frequency separation between the lines in each of the above pairs [equal to $2\sqrt{(\delta^2-\xi^2)}$] becomes smaller and smaller and approaches zero as ξ/δ approaches 1. On the contrary, the separation between the lines corresponding to the second (fourth) and the third resonances [in (6.52)] which is equal to $|\Delta_\ell+\sqrt{(\delta^2-\xi^2)}|$ increases as ξ/δ approachs 1 for any given $\Delta_\ell<0$. Hence one can say that these lines dynamically recede from each other, or unmix, as ξ/δ approaches unity. At $\xi/\delta=1$, the mixing (or unmixing) of lines has reached a maximum, and we have just three lines at

$$\Omega = \Delta_\ell \ , \ 0 \ , \ -\Delta_\ell \qquad (6.53)$$

with widths $\gamma+\sigma$, 2γ and $\gamma+\sigma$ respectively, since in the limit $\xi/\delta=1$, Eq.(6.51) reduces to

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s) \propto \frac{1}{(\Omega-2i\gamma)(\Omega-\Delta_\ell-i(\gamma+\sigma))}\left(\frac{1}{\Delta_\ell+i(\gamma+\sigma)}-\frac{1}{\Omega+\Delta_\ell-i(\gamma+\sigma)}\right). \qquad (6.54)$$

For $\xi/\delta > 1$, each of the resonances $\Omega=\Delta_\ell$ and $\Omega= -\Delta_\ell$ in (6.53) corresponds to a pair of lines with widths $\gamma+\sigma\pm\sqrt{(\xi^2-\delta^2)}$. Hence, as in the linear absorption spectrum, as ξ/δ increases beyond 1, the lines centred at $\Omega=\pm\Delta_\ell$ become narrower and narrower. In the limit, $\xi/\delta \sim \sigma/\delta >> 1$, one has

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s) \propto \frac{1}{(\Omega-\Delta_\ell-i\gamma)(\Delta_\ell+i\gamma)(\Omega+\Delta_\ell-i\gamma)} \qquad (6.55)$$

Hence in this limit, the extra resonance at $\Omega=0$ disappears, and the two lines centred at $\Omega=\pm\Delta_\ell$ become narrowed to a width approaching natural linewidth. It is also interesting to look at the case when there is no collisional coupling between the two components ($\sigma/\delta = \xi/\delta = 0$). In this limit, (6.51) reduces to

$$\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s) \propto \left\{ \frac{1}{(\Omega-\Delta_\ell-\delta-i\gamma)(\Delta_\ell+\delta+i\gamma)(\Omega+\Delta_\ell+\delta-i\gamma)} + \delta \leftrightarrow -\delta \right\}, \tag{6.56}$$

which is just the sum of $\chi^{(3)}$'s for two independent two-level systems. Note that the extra resonance at $\Omega=0$ now disappears, so that one has only four resonances, in general, at

$$\Omega = \Delta_\ell - \delta \ , \ \Delta_\ell + \delta \ , \ -(\Delta_\ell + \delta) \ , \ -(\Delta_\ell - \delta) \tag{6.57}$$

In Figs.11-14, we plot the FWM signal $|\chi^{(3)}(\omega_\ell,\omega_\ell,-\omega_s)|^2$ vs. $\Omega(=\omega_s-\omega_\ell)$ for various values of pump detuning and crossrelaxation rates $\xi(=\sigma)$. Fig.11 shows the usual FWM signal in the absence of collisional coupling between the two components ($\xi/\delta = \sigma/\delta = 0$). In Figs.12-14, we display the changes in the FWM signals as the strength of the collisions increases. We show results both with and without crossrelaxation. When all the five lines are resolved, then crossrelaxation reduces the strength of the collision-induced coherence at $\Omega=0$. This can be understood from the fact that the sign of ξ in the numerator in $g_2(\xi)$ [which is the same as $g_1(\xi)$ except for Δ_s and Δ_ℓ interchanged] is opposite to that of σ. In particular for large detunings, $\Delta_\ell \sim \Delta_s = \Delta >> \gamma,\sigma,\xi$, we have

$g_2(\xi) \sim 4i(\sigma-\xi)/\Delta^2$ so that the pressure-induced extra resonance at $\Omega=0$ disappears if $\sigma=\xi$. Hence the crossrelaxation ξ tends to decrease the strength of the collision-induced (i.e., σ-induced) resonance at $\Omega=0$. The effect of crossrelaxation is seen to be more dramatic when the pump is detuned far away from the resonance frequencies of either of the two components.

Thus, in conclusion, we have studied the effect of crossrelaxation on saturated absorption and four-wave mixing. We have based our calculations on the general atomic relaxation equations which follow by considering the interaction of the atoms with the bath of perturbers. Crossrelaxation makes a difference in the pump-induced asymmetry in the third-order absorption spectrum. The effect of crossrelaxation on four-wave mixing is more dramatic than on saturated absorption. Line mixing and line narrowing occur in four-wave mixing as well, as in the linear absorption spectrum. Further, crossrelaxation is found to reduce the strength of the pressure-induced resonances in these spectra.

CHAPTER VII

RENORMALIZATION OF THE NONLINEAR SUSCEPTIBILITIES DUE TO INTENSE PUMPS

In Chapter II, we had developed a nonlinear response theory that was valid under arbitrary relaxation conditions. However we had assumed that the external fields were weak so that one could use a perturbative analysis and compute the response functions to some n^{th} order in the weak external fields. Such a perturbative analysis is generally valid if the typical detunings from atomic frequencies are far bigger than the typical Rabi frequencies ($\sim|\vec{d}.\vec{E}/\hbar|$) 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 have to be treated to all orders. The remaining fields can however be treated perturbatively. In this chapter, we develop the nonlinear response theory when some of the applied fields are strong while the other fields are weak. We will work in the dressed-state basis and make use of the dressed-atom approximation[33] which is generally valid for strong fields. The dynamical equations in the dressed-state representation, when the dressed-atom approximation is made, have the same structure as in the absence of the strong fields, except that now the various parameters that appear in the equations of motion are dependent on the strength of the strong field. Hence the nonlinear response theory for a system dressed by one or more

strong fields can be developed on the lines of the nonlinear response theory developed in Chapters II-IV which was valid in the absence of the strong fields. In particular, one can obtain the n^{th} order nonlinear susceptibility $\chi^{(n)}$ of a strong-field-dressed system (n^{th} order in the weak external fields) from the nonlinear susceptibility $\chi^{(n)}$ of a bare atom by a simple renormalization (or re-identification) of the various parameters that appear in the equations of motion in the dressed-state picture. Equivalently, the diagrammatic method of calculation of the nonlinear susceptibilities developed in Chapter III can be utilized to compute the nonlinear susceptibilities of a strong-field-dressed system too, except that now the terms corresponding to the various diagrams involve the renormalized (strong-field-dependent) parameters. The intensity-dependent susceptibilities to various orders in the weak external fields explain various phenomena[16-18] that occur in presence of the strong fields. For example, the intensity-dependent linear susceptibility of a two-level atom shows resonances at the Rabi frequency of the strong field,while the higher order intensity-dependent susceptibilities show resonances at various submultiples of the Rabi frequency. In Section II, we develop a Liouville operator formulation of the nonlinear response theory of a system which is dressed by one or more strong fields and which is undergoing arbitrary relaxation. We work in the dressed-state basis and make use of the dressed-atom approximation. We calculate explicitly the various intensity-dependent parameters for the case of a two-level atom dressed by a strong field. In subsequent sections, we examine the effect of strong-

field dressing on the first, second and third-order response of a two-level atom.

II. NONLINEAR RESPONSE THEORY WITH SATURATING FIELDS

Consider a system undergoing relaxation and interacting with external fields, same of which are strong and some of which are weak. The dynamics of atom-field interaction is described by (2.2) which we rewrite as

$$\frac{\partial \rho}{\partial t} = -i[H_o \rho] - i[V(t) + F(t), \rho] + L_R \rho \quad , \tag{7.1}$$

where L_R is the relaxation part of $L_o = L_R - i[H_o, \ ]$ and $V(t)[F(t)]$ represents the interaction with the strong [weak] fields. We make a canonical transformation

$$U^{-1}(t) \, [H_o + V(t) \,] \, U(t) = \tilde{H}_o \quad , \tag{7.2}$$

such that $\tilde{H}_o$ is time-independent. As a result of the canonical transformation, (7.1) transforms into

$$\frac{\partial \tilde{\rho}}{\partial t} = -i[\, \tilde{h} \, , \, \tilde{\rho} \,] - i[\, \tilde{F}(t), \, \tilde{\rho} \,] + L_R \, \tilde{\rho} \quad , \tag{7.3}$$

where

$$\tilde{h} = \tilde{H}_o + i \, \frac{\partial U^{-1}}{\partial t} \, U \quad ,$$

$$\tilde{F}(t) = U^{-1}(t)\, F(t) U(t) \qquad (7.4)$$

Note that a U(t) as in (7.2) can always be chosen provided one neglects the counter-rotating terms in V(t) and provided no two strong fields saturate the same transition.[17,72,73] The choice of U(t) will depend on the structure of the energy levels and the external strong fields. Now one can make one more canonical transformation and go to a basis in which $\tilde{h}$ is diagonal

$$S^{-1}\, \tilde{h}\, S = \beta \;, \quad \tilde{h}|\beta_i\rangle = \beta_i |\beta_i\rangle \;. \qquad (7.5)$$

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.[33] Note that the conventional dressed-state description[32] uses the quantized version of the external fields, whereas here we treat the fields classically.[17,72,73] The eigenstates $|\beta_i\rangle$ are the superpositions of the eigenstates of H_o with expansion coefficients that depend on the strength of the strong field. We now transform (7.3) to the basis in which $\tilde{h}$ is diagonal. On defining

$$\tilde{\tilde{\rho}} = S^{-1}\, \tilde{\rho}\, S \;, \quad \tilde{\tilde{F}}(t) = S^{-1}\, \tilde{F}(t) S \;, \qquad (7.6)$$

Eq.(7.3) leads to

$$\frac{\partial \tilde{\tilde{\rho}}}{\partial t} = -i[\beta, \tilde{\tilde{\rho}}] - i[\tilde{\tilde{F}}(t), \tilde{\tilde{\rho}}] + S^{-1}[L_R(S\, \tilde{\tilde{\rho}}\, S^{-1}]S \;. \qquad (7.7)$$

The relaxation terms in (7.7) acquire a simple structure if one

makes the dressed-atom approximation,[33,17,72,73] which consists of using

$$\langle\beta_i|S^{-1}[L_R(S\,\tilde{\tilde{\rho}}\,S^{-1})]S|\beta_j\rangle$$

$$= -q_{ij}(1-\delta_{ij})\,\tilde{\tilde{\rho}}_{ij} + \delta_{ij}\sum_k \left(p_{ik}\,\tilde{\tilde{\rho}}_{kk} - p_{ki}\,\tilde{\tilde{\rho}}_{ii} \right)$$

$$= L_D\,\tilde{\tilde{\rho}} \quad . \tag{7.8}$$

Note that q_{ij} and p_{ij} are strong-field dependent relaxation parameters. In the dressed-atom approximation, Eq.(7.7) reduces to

$$\frac{\partial\tilde{\tilde{\rho}}}{\partial t} = -i[\beta,\,\tilde{\tilde{\rho}}\,] - i[\,\tilde{\tilde{F}}(t)\,,\,\tilde{\tilde{\rho}}] + L_D\,\tilde{\tilde{\rho}} \quad . \tag{7.9}$$

Hence if we work in the dressed-state basis and make the dressed-atom approximation, then the basic dynamical equation (7.9) has the same structure as that of (2.2) which was used in the perturbative calculations. Thus the density matrix $\tilde{\tilde{\rho}}$ to n^{th} order in $\tilde{\tilde{F}}(t)$ can be obtained from Eq.(2.22). The response of the observable Q can be written as

$$Q(t) = \mathrm{Tr}\left\{ \rho(t)Q \right\} = \mathrm{Tr}\left\{ \tilde{\tilde{\rho}}(t)\tilde{\tilde{Q}}(t) \right\} \quad ,$$

$$\tilde{\tilde{Q}}(t) = S^{-1}\,U^{-1}(t)QU(t)S \tag{7.10}$$

Thus the n^{th} order nonlinear response of the observable Q will be given by Eq.(2.25) with

$$Q \to \tilde{\tilde{Q}}(t) \quad , \; L_o \to L_D - i[\beta, \;\;] \quad , \tag{7.11}$$

$$-i[\, \tilde{\tilde{F}}(t), \;\;] \;=\; \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega \; e^{-i\Omega t} \; L_f(\Omega) \quad . \tag{7.12}$$

If we write

$$\tilde{\tilde{Q}}(t) \;=\; \sum_{a}^{-} Q_a \; e^{-i\omega_a t} \quad , \; \tilde{\tilde{F}}(\Omega) \;=\; -\sum_{\alpha}^{-} f_\alpha(\Omega) \; s_\alpha \quad , \tag{7.13}$$

then, the nonlinear response follows from Eqs.(2.25) and (2.26).

$$Q^{(n)}(t) \;=\; \sum^{-} \left(\frac{1}{2\pi} \right)^n \int_{-\infty}^{\infty} d\Omega_1 \ldots \int_{-\infty}^{\infty} d\Omega_n \; e^{-it(\omega_a + \sum_l \Omega_l)}$$

$$\times \;\; I\chi^{(n)}_{a\{\alpha_n\}}(\{\Omega_n\}) \; f_{\alpha_1}(\Omega_1) \ldots f_{\alpha_n}(\Omega_n) \quad , \tag{7.14}$$

where

$$I\chi^{(n)}_{a\{\alpha_n\}}(\{\Omega_n\}) \;=\; \frac{N(-i)^n}{n!} \; \text{sym Tr} \left\{ Q_a \left(\sum_l \Omega_l - iL_o \right)^{-1} L_{\alpha_1} \right.$$

$$\left. \left(\sum_{l=2}^{n} \Omega_l - iL_o \right)^{-1} L_{\alpha_2} \ldots (\Omega_n - iL_o)^{-1} L_{\alpha_n} \tilde{\tilde{\rho}}(o) \right\} \; , \; L_{\alpha_n} = -i[s_{\alpha_n}, \;\;] \; . \tag{7.15}$$

Note that the subscript I to the left of $\chi^{(n)}$ in (7.15) implies that the n^{th}-order susceptibility is intensity-dependent. The intensity dependence arises because the new Liouville operators L_o

and L_α [Eqs.(7.11),(7.12)] depend on the strength of the saturating fields. Thus the equation (7.15) gives the nonlinear response of a system whose states are dressed by some saturating fields. The explicit expression for nonlinear response of a bare atom to various orders in the external fields (Chapters II-IV) can be easily translated into the dressed-atom case to yield the intensity-dependent susceptibilities, if one keeps in view the transformation (7.12) and uses the following translation table:

$$\gamma_{ij} \rightarrow p_{ij} \quad , \quad \Gamma_{ij} \rightarrow q_{ij} \quad ,$$

$$\Lambda_{ij} \rightarrow \tilde{\Lambda}_{ij} = \beta_i - \beta_j - iq_{ij} \, ,$$

$$\rho_{ii}^{(o)} \rightarrow \tilde{\rho}_{ii}^{(o)} \qquad (7.16)$$

However, it should be remembered that the frequencies $\Omega_1, \Omega_2, \ldots$ in (7.15) are not the frequencies of the external weak field but that these involve the combinations of the weak-field and the strong-field frequencies, because of the transformation (7.12). It should also be remembered that the indices $\alpha_1, \alpha_2, \ldots$, in (7.14),(7.15) need not refer to the cartesian components of the weak field. They could simply denote the various terms that occur in the expansion of $\tilde{F}(\omega)$ [Eq.(7.13)].

In order to understand the abstract formulation given above, we consider the interaction of a two-level system with two external fields of frequencies ω_1 and ω_2 and wave vectors $\vec{k}_1$ and

$\vec{k}_2$. We assume that the field ω_1 is strong and that ω_2 is weak. The various parts of the Hamiltonian are

$$H_o = \frac{\omega_o}{2}\left(A_{11}-A_{22} \right)$$

$$V(t) = GA_{12}\, e^{-i\omega_1 t} + h.c. \;, \quad G = -\vec{d}_{12}\cdot\vec{e}_1\, e^{i\vec{k}_1\cdot\vec{r}} \;,$$

$$F(t) = -d_{12}e_2A_{12}\, e^{-i\omega_2 t} + h.c. \;, \quad d_{12} = \vec{d}_{12}\cdot\hat{e}_2 e^{i\vec{k}_2\cdot\vec{r}} \qquad (7.17)$$

where we have defined the operator A_{ij} as

$$A_{ij} = |i\rangle\langle j| \qquad (7.18)$$

The canonical transformation with

$$U(t) = e^{-i\omega_1 t(A_{11}-A_{22})/2} \;; \qquad (7.19)$$

will lead to

$$\tilde{h} = \frac{\Delta}{2}\left(A_{11}-A_{12} \right) + GA_{12} + h.c., \; \Delta = \omega_o-\omega_1$$

$$\tilde{F}(t) = -d_{12}e_2A_{12}\, e^{-i\delta t} + h.c. \;, \quad \delta = \omega_2-\omega_1 \qquad (7.20)$$

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

$$\beta_{1,2} = \pm \frac{\Omega_R}{2} \quad , \quad \Omega_R = \sqrt{(\Delta^2+4|G|^2)} \quad ,$$

$$S = \begin{pmatrix} \cos\theta & -e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & \cos\theta \end{pmatrix} ,$$

$$|\beta_1\rangle = \begin{pmatrix} \cos\theta \\ e^{i\phi}\sin\theta \end{pmatrix} \quad , \quad |\beta_2\rangle = \begin{pmatrix} -e^{-i\phi}\sin\theta \\ \cos\theta \end{pmatrix} ,$$

$$\tan\theta = \frac{2|G|}{\Delta+\Omega_R} \quad , \quad G = |G|e^{-i\phi} \tag{7.21}$$

On making one more canonical transformation with S, we get

$$\tilde{\tilde{F}}(t) = -\tilde{d}^{+}e_1 \, e^{-i\delta t} + \text{h.c.} \quad , \quad (\tilde{d}^{+})^{+} = \tilde{d}^{-} \tag{7.22}$$

where $\tilde{d}^{+} = d_{12}(S^{-1}A_{12}S)$

$$= d_{12}\Big(e^{i\phi}\sin\theta\cos\theta|1\rangle\langle 1| + \cos^2\theta|1\rangle\langle 2|$$

$$- e^{2i\phi}\sin^2\theta|2\rangle\langle 1| - e^{i\phi}\sin\theta\cos\theta|2\rangle\langle 2| \Big) \quad . \tag{7.23}$$

Hence on using (7.22) in (7.13), it follows that

$$\tilde{\tilde{F}}(\Omega) = f_{+}(\Omega)\tilde{d}^{+}+f_{-}(\Omega)\tilde{d}^{-} \equiv \sum_{\alpha}^{-} f_{\alpha}(\Omega)s_{\alpha} \quad , \tag{7.24}$$

where

$$f_+(\Omega) = 2\pi e_2 \delta(\Omega-\delta)$$

$$f_-(\Omega) = 2\pi e_2^* \delta(\Omega+\delta) \qquad (7.25)$$

Note that the index α in (7.24) does not correspond to the cartesian component of the polarization of the field $\vec{\epsilon}_2$. The component of the induced polarization in the direction of the probe field, for instance, will then be

$$P(t) = Tr\{ d\rho \} = Tr\{ \overset{*}{d}(t)\, \overset{*}{\rho}(t) \} ,$$

$$\overset{*}{d}(t) = \tilde{d}^- e^{-i\omega_1 t} + \tilde{d}^+ e^{i\omega_1 t} \equiv \sum_a^- Q_a e^{-i\omega_a t} , \qquad (7.26)$$

where $\tilde{d}^{\pm}$ is given by (7.22). The relaxation terms (7.8) can be calculated by using (7.21) and these are found to be [Cf. Ref.33]

$$q_{12} = \frac{1}{2}(\gamma_{12}+\gamma_{21})(1+2\sin^2\theta\cos^2\theta) + \Gamma_{12}^{ph}(1 - 2\sin^2\theta\cos^2\theta) ,$$

$$p_{12} = \gamma_{21}\sin^4\theta + \gamma_{12}\cos^4\theta + 2\Gamma_{12}^{ph}\sin^2\theta\cos^2\theta ,$$

$$p_{21} = \gamma_{21}\cos^4\theta + \gamma_{12}\sin^4\theta + 2\Gamma_{12}^{ph}\sin^2\theta\cos^2\theta \qquad (7.27)$$

Multilevel systems can be dealt with in an analogous manner. Next we examine the effects of strong-field dressing on the linear and nonlinear susceptibilities of a two-level atom.

III. EFFECTS OF DRESSING ON FIRST-ORDER RESPONSE

It follows from Eqs.(7.14)-(7.15) that the response of a dressed system to first order in the weak field is given by

$$Q^{(1)}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega \sum_{a}^{-} e^{-it(\omega_a+\Omega)} \, {}_{I}\chi^{(1)}_{a\alpha}(\Omega) \, f_{\alpha}(\Omega) \quad , \tag{7.28}$$

where

$${}_{I}\chi^{(1)}_{a\alpha}(\Omega) = N(-i) \, Tr \left\{ Q_a (\Omega - iL_o)^{-1} L_{\alpha} \tilde{\tilde{\rho}}^{(o)} \right\} \quad , \tag{7.29}$$

and Q_a, L_o and L_α are given by (7.11)-(7.13). The expression in (7.29) can be written in an explicit form as

$${}_{I}\chi^{(1)}_{a\alpha}(\Omega) = N\left(\tilde{\tilde{\rho}}^{(o)}_{ii} - \tilde{\tilde{\rho}}^{(o)}_{jj} \right) \left[Q_a \right]_{ji} \left[s_{\alpha} \right]_{ij} \left[\Omega - \tilde{\Lambda}_{ij} \right]^{-1}$$

$$\tilde{\Lambda}_{ij} = \beta_i - \beta_j - iq_{ij} \quad . \tag{7.30}$$

Here the β's refer to the energies of the dressed-states, q_{ij} is the intensity-dependent relaxation rate of the off-diagonal element of ρ in the dressed -state basis. The $\tilde{\tilde{\rho}}^{(o)}_{ii}$ refer to the populations of the dressed-states. Note that the expression in (7.30) can be obtained simply by a renormalization of the bare atom linear susceptibility (2.39), i.e., by letting $d^{\mu} \to Q_a$, $d^{\alpha} \to s_{\alpha}$ and by using the translation table (7.16). As a special case, the induced polarization of a dressed two-level system can be obtained

from (7.28)-(7.30) by making use of the relations (7.23) and (7.26). We have shown that $P^{(1)}(t)$ $[=\vec{P}^{(1)}(t).\hat{e}_2]$ can be written as

$$P^{(1)}(t) = e^{-i(\omega_1+\delta)t}\, {}_I\chi^{(1)}_{abs}(\delta)e_2 + e^{-i(\omega_1-\delta)t}\, {}_I\chi^{(1)}_{FWM}(-\delta)e_2^* + h.c. \quad , \tag{7.31}$$

where

$${}_I\chi^{(1)}_{abs}(\delta) = N\left(\tilde{\tilde{\rho}}^{(o)}_{11} - \tilde{\tilde{\rho}}^{(o)}_{22}\right)\left[\frac{\tilde{d}^+_{12}\tilde{d}^-_{21}}{\delta-\tilde{\Lambda}_{12}} - \frac{\tilde{d}^-_{12}\tilde{d}^+_{21}}{\delta-\tilde{\Lambda}_{21}}\right] \quad , \tag{7.32}$$

$${}_I\chi^{(1)}_{FWM}(-\delta) = N\left(\tilde{\tilde{\rho}}^{(o)}_{11} - \tilde{\tilde{\rho}}^{(o)}_{22}\right)\left[\frac{\tilde{d}^-_{12}\tilde{d}^-_{21}}{-\delta-\tilde{\Lambda}_{12}} - \frac{\tilde{d}^-_{12}\tilde{d}^-_{21}}{-\delta-\tilde{\Lambda}_{21}}\right] \quad ,$$

$$\tilde{\Lambda}_{12} = \Omega_R - iq_{12} \quad , \quad \tilde{\Lambda}_{21} = -\Omega_R - iq_{12} \quad , \quad \delta=\omega_2-\omega_1 \quad . \tag{7.33}$$

Note that the intensity-dependent susceptibility ${}_I\chi^{(1)}_{abs}(\delta)$ [or ${}_I\chi^{(1)}_{FWM}(-\delta)$] can be obtained from (7.30) by substituting $\tilde{d}^-$, $\tilde{d}^+$ and δ [or $\tilde{d}^-,\tilde{d}^-$ and $-\delta$] respectively in place of Q_a, s_α and Ω. The intensity-dependent susceptibilities ${}_I\chi^{(1)}_{abs}(\delta)$ and ${}_I\chi^{(1)}_{FWM}(-\delta)$ respectively describe absorption at frequency ω_2 and generation of radiation of frequency $2\omega_1-\omega_2$ under conditions when the field ω_1 is strong. Hence it is clear from Eqs.(7.32)-(7.34) that both in absorption as well as in four-wave mixing, there appear resonances at $\delta=\omega_2-\omega_1 = \pm\,\Omega_R$ with a width q_{12}. This explains the resonances at Rabi frequency in non-degenerate four-wave mixing. The populations

$\tilde{\rho}^{(o)}_{ii}$ are in general determined in terms of the relaxation parameters p_{ij}. For the two-level system we have

$$\tilde{\rho}^{(o)}_{11} = \frac{p_{12}}{p_{12}+p_{21}} \quad , \quad \tilde{\rho}^{(o)}_{22} = \frac{p_{21}}{p_{12}+p_{21}} \tag{7.35}$$

The contribution (7.33) can also be used for studying the transfer of modulation[74] from a probe beam to a saturating beam. For this purpose, assume that the probe beam has components ω_2, $\omega_2 \pm \Omega_m$. Hence we write the weak-field interaction as

$$F(t) = - d_{12}e_2\left[e^{-i\omega_2 t} + \frac{M}{2} e^{-i(\omega_2+\Omega_m)t} \pm \frac{M}{2} e^{-i(\omega_2-\Omega_m)t} \right] A_{12} + h.c. \tag{7.37}$$

where M and Ω_m are respectively the modulation depth and modulation frequency of the probe field. The + and - sign in (7.37) refer respectively to an amplitude-modulated and a frequency-modulated probe. The total induced polarization will be obtained by summing over the contributions from each probe frequency. The induced polarization describing four-wave mixing can be written as

$$P^{(1)}_{FWM}(t) = \left\{ e^{-(\omega_1-\delta)t} \; {}_I\chi^{(1)}_{FWM}(-\delta) e_2^* + e^{-i(\omega_1-\delta-\Omega_m)t} \right.$$

$$\left. \times \; {}_I\chi^{(1)}_{FWM}(-\delta-\Omega_m) \frac{M}{2} e_2^* \pm e^{-i(\omega_1-\delta+\Omega_m)t} \; {}_I\chi^{(1)}_{FWM}(-\delta+\Omega_m) \frac{M}{2} e_2^* \right\} + c.c. \tag{7.38}$$

where ${}_I\chi^{(1}_{FWM}(-\delta)$ is given by (7.33). Note that ${}_I\chi^{(1)}_{FWM}(-\delta-\Omega_m)$ and ${}_I\chi^{(1)}_{FWM}(-\delta+\Omega_m)$ will have resonances at $-\delta=\pm\Omega_R+\Omega_m$ and $-\delta=\pm\Omega_R-\Omega_m$ respectively. Thus when $\omega_2=\omega_1$ (i.e., $\delta=0$) (7.38) becomes

$$P^{(1)}_{FWM}(t) = \left\{ e^{-i\omega_1 t}\, {}_I\chi^{(1)}_{FWM}(o)\, e_2^* + e^{-i(\omega_1-\Omega_m)t}\, {}_I\chi^{(1)}_{FWM}(-\Omega_m)\, \frac{M}{2}\, e_2^* \right.$$

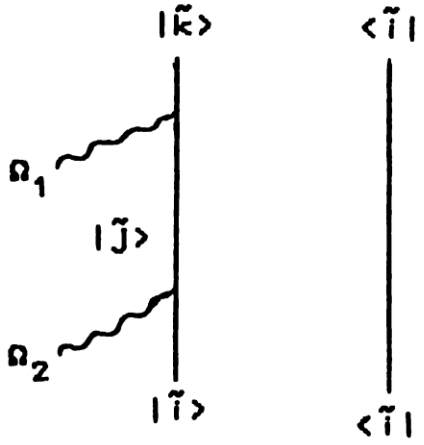
$$\left. \pm e^{-i(\omega_1+\Omega_m)t}\, {}_I\chi^{(1)}_{FWM}(\Omega_m)\, \frac{M}{2}\, e_2^* \right\} + c.c. \qquad (7.39)$$

Note that the induced polarization given by (7.39) will act as a source term in (1.2) to generate a modulated field of frequency ω_1 with the modulation depth and modulation frequency given by M and Ω_m respectively. Thus it is clear from (7.39) that when $\omega_2=\omega_1$, there occurs a transfer of modulation from the probe (7.37) to the pump and this modulation transfer will be maximum[74] when $\Omega_m = \pm\Omega_R$.

IV. DIAGRAMMATIC CALCULATION OF INTENSITY-DEPENDENT SUSCEPTIBILITIES

In this section, we explain how the diagrammatic method described in Chapter III can be used for the calculation of the intensity-dependent susceptibilities that describe the nonlinear response of a system dressed by one or more strong fields. The structure of the diagrams for the case of a dressed system is essentially the same as in the bare-atom case. The terms corresponding to the diagrams are different, but they can be obtained simply from the bare-atom terms by letting $d^{\mu}\to Q_a$, and $d^{\alpha}, d^{\beta}, \ldots$

$\rightarrow s_\alpha, s_\beta, \ldots$ and using the translation table (7.16). Consider for instance the following diagram:

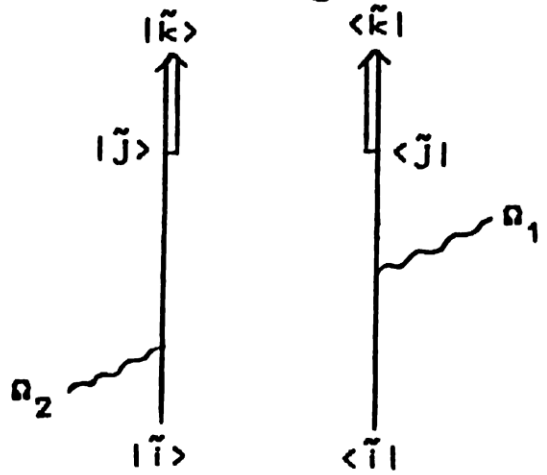


Note that we have used the 'tilde' symbol to denote the dressed states, e.g., $|\tilde{i}\rangle$. Following the method described in Chapter III, the term corresponding to the above diagram can be written as

$$T = (-1)^2 \frac{\tilde{\tilde{\rho}}^{(o)}_{ii} (Q_a)_{ik} (s_\alpha)_{kj} (s_\beta)_{ji}}{(\Omega_1+\Omega_2-\tilde{\Lambda}_{ki})(\Omega_2-\tilde{\Lambda}_{ji})} \quad . \qquad (7.40)$$

Note that the expression in (7.40) will correspond to a term in the second-order intensity-dependent susceptibility $_I\chi^{(1)}_{a\alpha\beta}(\Omega_1,\Omega_2)$. The quantities $\tilde{\tilde{\rho}}^{(o)}_{ii}$ and $\tilde{\Lambda}_{ij}$ refer respectively to the population of the initial dressed-state and the complex atomic frequencies ($\tilde{\Lambda}_{ij} = \beta_i-\beta_j-iq_{ij}$) of the dressed system. The quantities Q_a and s_α are defined by Eq.(7.13). It should be remembered that Ω_1,Ω_2 here do refer not to the weak-field frequencies but rather to the combinations of the strong-field and the weak-field frequencies. For example in the case of a two-level atom interacting with a strong field ω_ℓ and a weak probe ω_s, Ω_1 and Ω_2 can take the values $\pm(\omega_s-\omega_\ell)$. Further, the inelastic contributions too are important for the nonlinear response of a dressed system. The following is

an example of an inelastic diagram.



Note that the double lines in the above diagram refer to the fact that a transfer of population from the dressed-state $|\tilde{j}\rangle$ to $|\tilde{k}\rangle$ has taken place after the dressed system has interacted with the two fields Ω_1 and Ω_2. The term corresponding to the above inelastic diagram would then be

$$T = (-1)^2 \frac{\tilde{\tilde{\rho}}^{(0)}_{ii} (Q_a)_{kk} (-s_\alpha)_{ij} (s_\beta)_{ji}}{\Omega_2 - \tilde{\Lambda}_{ji}} B_{jk}(\Omega_1+\Omega_2) \quad , \tag{7.41}$$

where $B_{jk}(\Omega)$ is now defined as

$$B_{jk}(\Omega) = \sum_{\ell}^{-} \frac{\tilde{S}^{-1}_{\ell j} \tilde{S}_{k\ell}}{\Omega - i\tilde{\lambda}_\ell} \tag{7.42}$$

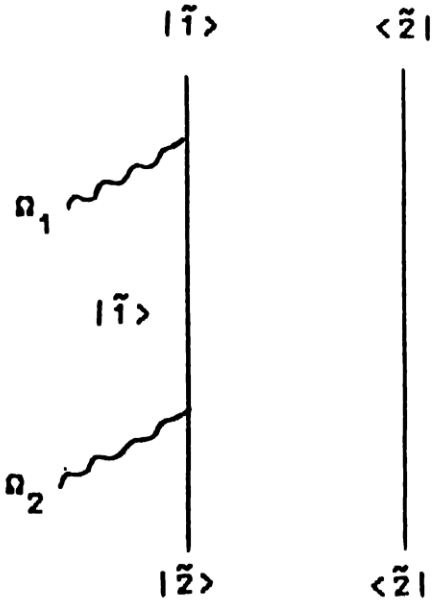
Here $\tilde{S}$ is the matrix that diagonalizes the population relaxation matrix $\tilde{R}$ of the dressed system [$\tilde{R}_{ij} = p_{ij} (i \neq j)$, $\tilde{R}_{ii} = -\sum_k p_{ki}$], i.e., $\tilde{S}^{-1}\tilde{R}\tilde{S} = \tilde{\lambda}, \tilde{\lambda}_{ij} = \delta_{ij}\tilde{\lambda}_i$. Thus following the diagrammatic method of Chapter III, diagrams such as above can be written down that will yield all the terms in the second-order intensity-dependent susceptibility ${}_I\chi^{(2)}_{a\alpha\beta}(\Omega_1,\Omega_2)$ or in general, the terms in the n^{th} order intensity-dependent susceptibility ${}_I\chi^{(n)}_{a\{\alpha_n\}}(\{\Omega_n\})$ for any n.

V. SUBHARMONIC RESONANCES IN THE NONLINEAR RESPONSE OF A DRESSED SYSTEM

Using the general scheme outlined in Section II, we can also look at the higher-order intensity-dependent susceptibilities. For example, one can look at the susceptibilities which are of third order in the weak fields but which hold to all orders in some strong, near-resonant field. Some general features of such susceptibilities can easily be seen. For example, consider a system driven by a strong field ω_ℓ and a weak field ω_s. In the absence of the strong field, the bare-atom susceptibility $\chi^{(3)}(\omega_s,-\omega_s,\omega_s)$ will describe energy absorption from ω_s, to fourth-order in the weak field. Let the strong field saturate the optical transition $|1\rangle\leftrightarrow|2\rangle$. Then in order to obtain the intensity-dependent susceptibility, we have to replace, besides other things, ω_s by $\omega_s-\omega_\ell$ and Λ_{jn} by the complex atomic frequencies of the dressed system $\tilde{\Lambda}_{jn}=\beta_j-\beta_n-iq_{jn}$. In the general expression (2.47) for the third-order bare-atom susceptibility. It is clear from the structure of (2.47) that such an intensity-dependent susceptibility will not only have a resonant structure when $\omega_s-\omega_\ell$ is equal to the Rabi frequency ($\sim\beta_j-\beta_n$) but also at the subharmonics of the Rabi frequency. For example, resonances like $\Lambda_{jn}=\omega_1+\omega_3$ will lead to the resonances like $\beta_j-\beta_n=2(\omega_s-\omega_\ell)$ in the intensity-dependent susceptibility, and thus to a structure at half of the Rabi frequency. Thus the multiphoton resonances in the usual susceptibilities imply the existence of resonances at various submultiples of Rabi frequencies. Such subharmonic resonances in the intensity-

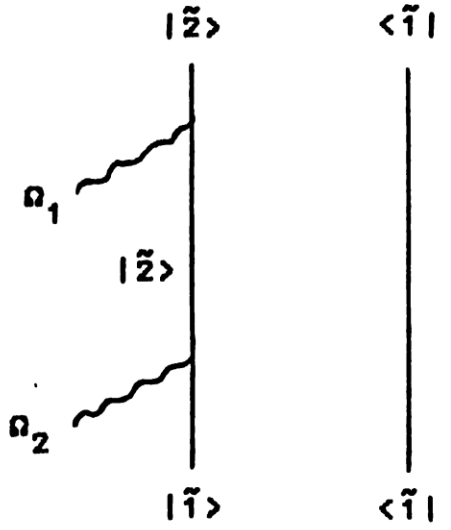
dependent susceptibilities have been extensively studied recently.[18] The above arguement shows that in general, the intensity-dependent susceptibilities obtained by a renormalization of the usual susceptibilities give us a qualitative understanding of such subharmonic resonances. In the following, we present a general discussion of the various subharmonic resonances that arise in the second-order and third-order intensity-dependent susceptibilities of a two-level atom interacting with a strong field ω_1 and weak field ω_2.

Consider a typical term in the second-order intensity-dependent susceptibility ${}_I\chi^{(2)}_{a\alpha\beta}(\Omega_1,\Omega_2)$, for example the term that is represented by the following diagram:



$$(-1)^2 \frac{\tilde{\tilde{\rho}}^{(0)}_{22}(Q_a)_{21}(s_\alpha)_{11}(s_\beta)_{12}}{(\Omega_1+\Omega_2-\tilde{\Lambda}_{12})(\Omega_2-\tilde{\Lambda}_{12})} . \quad (7.44)$$

Since $\tilde{\tilde{\rho}}^{(0)}_{11} \neq 0$, there will be a contribution to the second-order process described in the diagram in (7.44), from the following diagram as well.

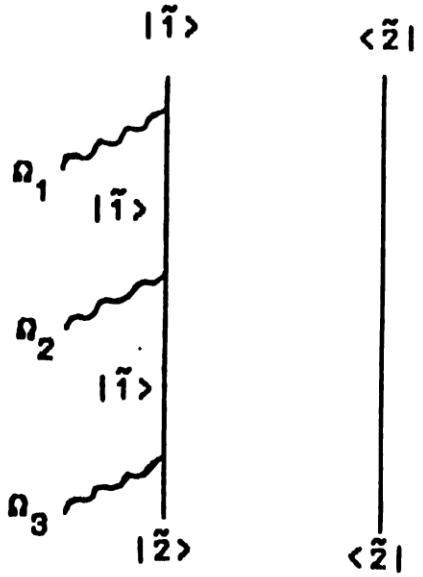


$$(-1)^2 \frac{\tilde{\rho}^{(o)}_{11}(Q_a)_{12}(s_\alpha)_{22}(s_\beta)_{21}}{(\Omega_1+\Omega_2-\tilde{\Lambda}_{21})(\Omega_2-\tilde{\Lambda}_{21})} \quad . \quad (7.45)$$

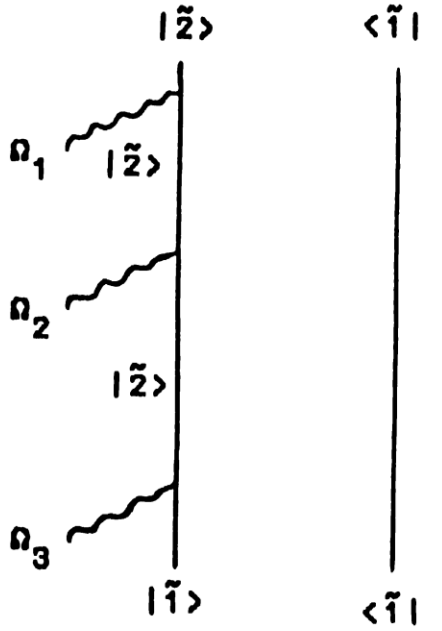
Note that in the expression in (7.44),(7.45), s_α and Q_a are as defined by (7.24) and (7.26) respectively, Ω_1 and Ω_2 can take the values $\pm\delta[=\pm(\omega_2-\omega_1)]$, and the complex atomic frequencies $\tilde{\Lambda}_{12},\tilde{\Lambda}_{21}$ are given by (7.33). Thus if we let $Q_a \rightarrow \tilde{d}^-$, $s_\alpha \rightarrow \tilde{d}^+$ [hence $\Omega_1=+\delta$] and $s_\beta \rightarrow \tilde{d}^+$ [hence $\Omega_2=+\delta$], then the terms in (7.44),(7.45) contribute to the induced polarization [Eqs.(7.14),(7.15)] oscillating at the frequency $\omega_a+\Omega_1+\Omega_2=\omega_1+\delta+\delta = 2\omega_2-\omega_1$. Thus it is clear from the expression (7.44),(7.45) that the signal generated at the frequency $2\omega_2-\omega_1$ [in the direction $2\vec{k}_2-\vec{k}_1$] exhibits not only the resonances at the Rabi frequency $\delta=\pm\Omega_R$ but also the subharmonic resonances $2\delta=\pm\Omega_R$. Similarly, if we let $Q_a \rightarrow \tilde{d}^-$, $(s_\alpha,\Omega_1)=(\tilde{d}^-,-\delta)$ and $(s_\beta,\Omega_2)=(\tilde{d}^-,-\delta)$, then the terms in (7.44),(7.45) contribute to the induced polarization oscillating at the frequency $\omega_1-\delta-\delta=3\omega_1-2\omega_2$. Hence it is evident from the structure of (7.44),(7.45) that the signal generated at the frequency $3\omega_1-2\omega_2$ [in the direction $3\vec{k}_1-2\vec{k}_2$] will also show the subharmonic resonances $\delta=\pm\Omega_R/2$.

We will now consider a typical term in the third-order intensity-dependent susceptibility ${}_I\chi^{(3)}_{a\alpha\beta\gamma}(\Omega_1,\Omega_2,\Omega_3)$ of a two-level

atom, say, a term that is determined by the contributions from the following diagrams:



$$(-1)^3 \frac{\tilde{\rho}^{(0)}_{22}(Q_a)_{21}(\varepsilon_\alpha)_{11}(\varepsilon_\beta)_{11}(\varepsilon_\gamma)_{12}}{(\Omega_1+\Omega_2+\Omega_3-\tilde{\Lambda}_{12})(\Omega_2+\Omega_3-\tilde{\Lambda}_{12})(\Omega_3-\tilde{\Lambda}_{12})}, \tag{7.46}$$



$$(-1)^3 \frac{\tilde{\rho}^{(0)}_{11}(Q_a)_{12}(\varepsilon_\alpha)_{22}(\varepsilon_\beta)_{22}(\varepsilon_\gamma)_{21}}{(\Omega_1+\Omega_2+\Omega_3-\tilde{\Lambda}_{21})(\Omega_2+\Omega_3-\tilde{\Lambda}_{21})(\Omega_3-\tilde{\Lambda}_{21})}, \tag{7.47}$$

It follows from (7.14),(7.15) that if we let $Q_a \to \tilde{d}^-$ and $(\varepsilon_\alpha,\Omega_1)=(\varepsilon_\beta,\Omega_2)=(\varepsilon_\gamma,\Omega_3)\to(\tilde{d}^+,\delta)$, then the terms in (7.46),(7.47) will give rise to a term in the induced polarization that oscillates at the frequency $\omega_1+3\delta=3\omega_2-2\omega_1$. Hence it is clear from (7.46,(7.47) that the signal generated at the frequency $3\omega_2-2\omega_1$ [in the direction $3\vec{k}_2-2\vec{k}_1$] exhibits the subharmonic resonances at $\delta=\pm\Omega_R/2$ as well as at $\delta=\pm\Omega_R/3$. On the other hand, if we let $Q_a\to\tilde{d}^-$, $(\varepsilon_\alpha,\Omega_1)\to(\tilde{d}^-,-\delta)$, $(\varepsilon_\beta,\Omega_2)=(\varepsilon_\gamma,\Omega_3)=(\tilde{d}^+,\delta)$, then it follows from (7.14),(7.15) that

the terms in (7.46),(7.47) contribute to the energy absorption from the probe ω_2. In this case one can see from the expressions in (7.46),(7.47) that there will be only the subharmonic resonances at $\delta=\pm\Omega_R/2$ and not at $\delta=\pm\Omega_R/3$. Thus it is clear from the above analysis that depending on the frequency and the direction of the generated signal that we look at, and depending on the strength of the probe field ω_2, we can observe the resonances at various submultiples of the Rabi frequency.

Thus, in conclusion, we have developed a formulation of nonlinear response of a system undergoing arbitrary relaxation and interacting with fields, some of which are strong while others are weak. We have shown how using the dressed-state representation and and the dressed-atom approximation one can obtain the intensity-dependent susceptibilities to various orders in the weak fields by doing a renormalization of the parameters occuring in the bare-atom expressions. The resonances in the intensity-dependent susceptibilities occur at the transition frequencies of the dressed system. In particular, the intensity-dependent linear susceptibility of a two-level atom interacting with a strong field and a weak field exhibits the resonances at the Rabi frequency of the strong field. Our result explains the phenomena of modulation transfer from the probe beam to the pump beam. We have also shown how the existence of the resonances at the submultiples of the Rabi frequency of the strong field in absorption and nonlinear mixing experiments can be understood from the structure of the resonant terms in the higher-order intensity-dependent susceptibilities.

CHAPTER VIII

TRANSIENT EFFECTS IN THE PRESENCE OF STRONG PUMPS

In Chapter VII, we have given a formulation of the steady-state nonlinear response of a system dressed by one or more strong fields. The intensity-dependent susceptibilities to various orders in the weak fields which could be obtained from the bare-atom expressions by a simple renormalization procedure enabled us to understand the resonances that occur at the Rabi frequency and at the submultiples of the Rabi frequency, in absorption and nonlinear mixing experiments.[18] In recent years, the transient response of systems with initial dressed-state preparation[34,75,76] has received a lot of attention in the literature. Mossberg et al[61] have shown how to prepare a system in a pure dressed state by using phase-controlled excitation. Mossberg and coworkers[34] have observed, for instance, that if one makes an observation at short times, then one of the peaks in the Autler-Townes spectrum is suppressed when the system is prepared initially in one of the dressed states. Thus in order to study the various phenomena that arise due to the intial dressed-state preparation, it is desirable to have a formulation of transient nonlinear response of a dressed system that is valid for arbitrary initial dressed-state conditions and for all time-scales of interest. In this chapter, we develop such a formulation of transient nonlinear response of dressed systems. We give a general expression for the time-dependent intensity-dependent susceptibility of an arbitrarily-

prepared system which is dressed by one or more strong fields and which is interacting with weak fields. We give the explicit result for the linear transient response of a dressed system. We specialize this result to a few situations where the initial dressed-state preparation gives rise to very interesting effects in the linear transient response. In particular, the transient suppression of one of the components of the Autler-Townes doublet of a system prepared initially in one of the dressed states, which was discovered recently by Mossberg and coworkers[34] can be easily understood from our results.

NONLINEAR TRANSIENT RESPONSE OF DRESSED SYSTEMS

Consider a system undergoing relaxation and interacting with fields, some of which are strong and some of which are weak. Let the initial state of the system be described by the density matrix in the dressed-atom picture, $\tilde{\tilde{\rho}}^{(o)}(0)$. The dynamics of atom-field interaction is described, an in (7.1), by the equation

$$\frac{\partial \rho}{\partial t} = -i\left[H_o, \rho\right] -i\left[V(t) + F(t), \rho\right] + L_R \rho \ , \qquad (8.1)$$

where L_R is the relaxation part of $L_o \equiv L_R - i[H_o, \ ]$ and V(t)[F(t)] represents the interaction with the strong [weak] fields. On making the various canonical transformations as in (7.2) and (7.6) and making the dressed-atom approximation (as in Chapter VII), Eq. (8.1) becomes

$$\frac{\partial \tilde{\tilde{\rho}}}{\partial t} = -i\left[\beta, \tilde{\tilde{\rho}} \right] - i\left[\tilde{\tilde{F}}(t), \tilde{\tilde{\rho}} \right] + L_D \tilde{\tilde{\rho}} \qquad (8.2)$$

where $L_D\tilde{\tilde{\rho}}$ [Eq.(7.8)] represents the relaxation of the dressed system, β is the Hamiltonian of the dressed system in the absence of the weak fields, and $\tilde{\tilde{F}}(t)$ represents the interaction of the dressed system with the weak fields. In view of the fact that the basic dynamical equation (8.2) in the dressed-state picture (when the dressed-atom approximation is made) has the same structure as that of (2.2) which was used in perturbative calculations (in the absence of the dressing field), the density matrix $\tilde{\tilde{\rho}}$ to n^{th} order in $\tilde{\tilde{F}}(t)$ can be obtained from Eq.(4.7). The time-dependent response of the observable Q can then be written as

$$Q(t) = Tr\left\{ \rho(t)Q \right\} = Tr\left\{ \tilde{\tilde{\rho}}(t)\, \tilde{\tilde{Q}}(t) \right\} ,$$

$$\tilde{\tilde{Q}}(t) = S^{-1}U^{-1}(t)QU(t)S . \qquad (8.3)$$

Thus the n^{th} order time-dependent nonlinear response of the observable Q will be given by (4.8) with

$$Q \rightarrow \tilde{\tilde{Q}}(t) \quad , \quad L_o \rightarrow L_D - i[\beta\ ,\ ] \ , \qquad (8.4)$$

$$-i[\tilde{\tilde{F}}(t),\ \ ] = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\Omega\ e^{-i\Omega t}\ \ L_F(\Omega) \qquad (8.5)$$

If we write

$$\tilde{\tilde{Q}}(t) = \sum_{a} Q_a e^{-i\omega_a t} \quad , \quad \tilde{\tilde{F}}(\Omega) = - \sum_{\alpha} f_{\alpha}(\Omega) e_{\alpha} \quad , \tag{8.6}$$

then, the time-dependent nonlinear response follows from Eq. (4.10) and (4.11). Thus we have

$$Q^{(n)}(t) = \sum \left(\frac{1}{2\pi} \right)^n \int_{-\infty}^{\infty} d\Omega_1 \ldots \int_{-\infty}^{\infty} d\Omega_n \, e^{-it\left(\omega_a + \sum_{i=1}^{n} \Omega_i\right)}$$

$$I\chi^{(n)}_{a\{\alpha_n\}} \left([\Omega_n], t \right) f_{\alpha_1}(\Omega_1) \ldots f_{\alpha_n}(\Omega_n) \tag{8.7}$$

where

$$I\chi^{(n)}_{a\{\alpha_n\}} \left([\Omega_n], t \right) = \frac{N(-1)^n}{n!} \, \mathrm{sym} \left(\frac{1}{2\pi i} \right) \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} dz \, e^{zt}$$

$$\mathrm{Tr}\Big\{ Q_a \Big(iz + \sum_{i=1}^{n} \Omega_i - iL_o\Big)^{-1} L_{\alpha_1} \Big(iz + \sum_{i=2}^{n} \Omega_i - iL_o\Big)^{-1} L_{\alpha_2}$$

$$\ldots (iz + \Omega_n - iL_o)^{-1} L_{\alpha_n} \big((iz - iL_o)^{-1} \tilde{\tilde{\rho}}^{(o)}(0) \Big\} \, , \; L_{\alpha_n} = -i[e_{\alpha_n},] \, . \tag{8.8}$$

Thus Eqs.(8.7)-(8.8) describe the n^{th} order transient response of a dressed system undergoing arbitrary relaxation and prepared in an initial state described by $\tilde{\tilde{\rho}}^{(o)}(0)$. The explicit expressions for the transient linear and nonlinear response of a bare atom to various orders in the external fields can be easily translated into the dressed-atom case to yield the time-dependent intensity-dependent susceptibilities if one keeps in view the transforma-

tion (8.5) and uses the translation table (7.16). We give below the result for the transient linear response of a dressed system which is prepared initially in a state described by $\tilde{\tilde{\rho}}^{(o)}(0)$. We have

$$Q^{(1)}(t) = \frac{1}{2\pi} \sum_{\alpha}^{-} \int_{-\infty}^{\infty} d\Omega \; e^{-i(\omega_a+\Omega)t} \; {}_I\chi^{(1)}_{a\alpha}(\Omega,t) \; f_\alpha(\Omega) \quad , \tag{8.9}$$

where

$${}_I\chi^{(1)}_{a\alpha}(\Omega,t) = {}_I\tilde{\Phi}^{(1)}_{a\alpha}(\Omega,t) + {}_I\Psi^{(1)}_{a\alpha}(\Omega,t) \quad , \tag{8.10}$$

and the two contributions ${}_I\tilde{\Phi}^{(1)}$ and ${}_I\Psi^{(1)}$ that arise respectively from the dressed-state populations $(\tilde{\tilde{\rho}}^{(o)}_{ii}(0))$ and the dressed-state coherences $(\tilde{\tilde{\rho}}^{(o)}_{ij}(0),\ i\neq j)$ are given by

$$\begin{aligned} {}_I\tilde{\Phi}^{(1)}_{a\alpha}(\Omega,t) = N \sum_{ijk}^{-} \Bigg\{ \sum_{\ell}^{-} \tilde{\tilde{\rho}}^{(o)}_{\ell\ell}(0)\, \tilde{S}^{-1}_{k\ell}\, \tilde{S}_{ik}\, e^{\tilde{\lambda}_k t} \Bigg[(s_\alpha)_{ij}(Q_a)_{ji} \\ \times \left[\frac{1-e^{i(\Omega-\tilde{\Lambda}_{ij}+i\tilde{\lambda}_k)t}}{\Omega-\tilde{\Lambda}_{ij}+i\tilde{\lambda}_k} \right] - (Q_a)_{ij}(s_\alpha)_{ji} \left[\frac{1-e^{i(\Omega-\tilde{\Lambda}_{ji}+i\tilde{\lambda}_k)t}}{\Omega-\tilde{\Lambda}_{ji}+i\tilde{\lambda}_k} \right] \Bigg] \Bigg\} , \end{aligned} \tag{8.11}$$

$$I\tilde{\Psi}^{(1)}_{a\alpha}(\Omega,t) = \tilde{\tilde{\rho}}^{(o)}_{lk}(0)(1-\delta_{lk})\, e^{-i\tilde{\Lambda}_{lk}t}$$

$$\times \left[(s_\alpha)_{kJ}(Q_a)_{Ji} \left(\frac{1 - e^{i(\Omega-\tilde{\Lambda}_{iJ}+\tilde{\Lambda}_{lk})t}}{\Omega - \tilde{\Lambda}_{iJ} + \tilde{\Lambda}_{lk}} \right) \right.$$

$$\left. - (Q_a)_{kJ}(s_\alpha)_{Ji} \left(\frac{1 - e^{i(\Omega-\tilde{\Lambda}_{Jk}+\tilde{\Lambda}_{lk})t}}{\Omega - \tilde{\Lambda}_{JK} + \tilde{\Lambda}_{lk}} \right) \right] . \qquad (8.12)$$

In Eq.(8.11), $\tilde{S}$ is the matrix that diagonalizes the dressed state population relaxation matrix $\tilde{R}$ [$\tilde{R}_{ik}=p_{ik}(i\neq k)$, $\tilde{R}_{ii}=-\sum_k p_{ki}$], i.e., $\tilde{S}^{-1}\tilde{R}\tilde{S}=\tilde{\lambda}$ ($\tilde{\lambda}=\tilde{\lambda}_i\delta_{ij}$). Equation (8.9) is the complete expression for the transient linear response of a dressed system. It can be seen from the expresssion (8.12) that there can be a new resonance at $\Omega=0$ in the linear transient response if the dressed states $|\tilde{j}\rangle$ and $|\tilde{k}\rangle$ are the same. Note that such a new resonance comes about because of the fact that the resonances in the linear transient response have the structure $(\Delta_1-\Delta_o)^{-1}$ [see Eq.(4.24)]. The contribution to the resonance at $\Omega=0$ from the relaxation terms is zero and hence such a resonance is characterized by a linewidth that is essentially determined by the interaction time t. Thus this resonance is of the same kind as the transient resonance that arises in nonlinear wave mixing in presence of weak pump and probe fields [as discussed in Chapter V]. As is apparent from the expression (8.12), the resonance at $\Omega=0$ can be present only if $\tilde{\rho}^{*(o)}_{ik}(0)\neq 0$ for $i\neq k$, i.e., only if there exists a coherence between dressed states $|\tilde{i}\rangle$ and $|\tilde{k}\rangle$ initially; and if the system is prepared initially in one

of the dressed states $|\tilde{\ell}\rangle$ so that $\rho^{s(o)}_{\ell\ell}(0)=1$, then the resonance at $\Omega=0$ would disappear. However, one must remember that the result (8.9)-(8.12) has been obtained under the dressed-atom approximation and is valid only in the limit of strong fields. We have verified that if one includes the nonsecular terms (terms which have been thrown away under the dressed-atom approximation) in the result (8.9), then the transient resonance is always present, whether or not there exists coherence between the dressed states initially. However, it is evident from the expression (8.12) that the transient resonance at $\Omega=0$ is suppressed in the limit of strong fields (i.e., when the dressed-atom approximation is valid) if the system is prepared initially in one of the dressed systems. Thus we have shown on very general grounds, how the new transient resonance that was shown to occur in nonlinear wave mixing in presence of weak fields in Chapters IV and V can be understood from the above result for the linear transient response of a dressed system. In section A below, we give a complete expression for the time-dependent intensity-dependent susceptibility of a two-level atom and discuss the various features of the transient resonance in the context of four-wave mixing. In section B we consider the application of the general result (8.9)-(8.12) to a situation where the initial dressed-state preparation gives rise to very interesting effects in the transient response of a dressed system. We show how the recently discovered transient suppression of one of the components of the Autler-Townes doublet follows from our general result.

A. Transient Linear Response of a Dressed Two-Level System

Consider a two-level system interacting with a strong field ω_1 and a weak probe ω_2. The various parameters in the dressed picture for this system have already been worked out explicitly in Chapter VII [Eqs.(7.21)-(7.27)]. We give here the general result for the linear time-dependent intensity-dependent susceptibility for this system, which follows from Eq.(8.9).

$$I\chi_{a\alpha}^{(1)}(\Omega,t) = 2a_{21}\tilde{\rho}_{11}^{(o)}(0)\left[(s_\alpha)_{12}(Q_a)_{21}\left(\frac{e^{\tilde{\lambda}_1 t} - e^{i(\Omega-\tilde{\Lambda}_{12})t}}{\Omega - \tilde{\Lambda}_{12} + i\tilde{\lambda}_1}\right)\right.$$

$$\left. - (Q_a)_{12}(s_\alpha)_{21}\left(\frac{e^{\tilde{\lambda}_1 t} - e^{i(\Omega-\tilde{\Lambda}_{21})t}}{\Omega - \tilde{\Lambda}_{21} + i\tilde{\lambda}_1}\right)\right]$$

$$+ a_{12}\left[(s_\alpha)_{12}(Q_a)_{21}\left(\frac{1 - e^{i(\Omega-\tilde{\Lambda}_{12})t}}{\Omega - \tilde{\Lambda}_{12}}\right)\right.$$

$$\left. - (Q_a)_{12}(s_\alpha)_{21}\left(\frac{1 - e^{i(\Omega-\tilde{\Lambda}_{21})t}}{\Omega - \tilde{\Lambda}_{21}}\right)\right]$$

$$+ \tilde{\rho}_{12}^{(o)}(0)\; e^{-i\tilde{\Lambda}_{12}t}\left[(s_\alpha)_{22}-(s_\alpha)_{11}\right)(Q_a)_{21}\left(\frac{1-e^{i\Omega t}}{\Omega}\right)$$

$$-(s_\alpha)_{12}\left[(Q_a)_{11}-(Q_a)_{22}\right)\left(\frac{1-e^{i(\Omega-i\tilde{\lambda}_1+\tilde{\Lambda}_{12})t}}{\Omega-i\tilde{\lambda}_1+\tilde{\Lambda}_{12}}\right)\Bigg] \qquad (8.13)$$

+ terms with $|1\rangle \leftrightarrow |2\rangle$,

where

$$\tilde{\lambda}_1 = -(p_{12}+p_{21}) \;,\; a_{12} = \frac{p_{12}}{p_{12}+p_{21}} \;,\; a_{21} = \frac{p_{21}}{p_{12}+p_{21}} \;,$$

$$\tilde{\Lambda}_{12} = \Omega_R - iq_{12} \;,\; \tilde{\Lambda}_{21} = -\Omega_R - iq_{12} \;,\; \Omega_R = \sqrt{(\Delta^2+4|G|^2)}. \qquad (8.14)$$

Equation (8.13) is the complete expression for the linear transient response of a dressed two-level system under arbitrary initial dressed-state conditions. As we have shown in Chapter VII [Eqs.(7.31)-(7.33)], the time-dependent intensity-dependent susceptibilities describing energy absorption from probe $\omega_2[{}_I\chi^{(1)}_{abs}(\delta,t)]$ and four-wave mixing $[{}_I\chi^{(1)}_{FWM}(-\delta,t)]$ can be obtained from Eq.(8.13) by replacing the set of parameters (Q_a, s_α, Ω) by $(\tilde{d}^-, \tilde{d}^+, \delta)$ and $(\tilde{d}^-, \tilde{d}^-, -\delta)$ respectively. The matrix elements of $\tilde{d}^{\pm}$ and the relaxation parameters p_{12}, p_{21}, q_{12} are as given by Eqs.(7.22) and (7.27) respectively. Berman et al[75] have made a detailed study of the transient probe spectra of a driven two-level system under various initial dressed-state conditions. Our

general result (8.13) with $Q_a \to \tilde{d}^-$, $(s_\alpha, \Omega) \to (\tilde{d}^+, \delta)$ is capable of yielding all the features that they have predicted in the transient probe absorption spectra under various initial conditions.

It can be seen from (8.13) that the four wave mixing (FWM) susceptibility ${}_I\chi^{(1)}_{FWM}(-\delta, t)$, for instance, shows a transient resonance at $\delta=\omega_2-\omega_1=0$. Consider, for simplicity, the system to be in the ground state initially, and consider only radiative relaxation ($\gamma_{12}=\Gamma^{ph}_{12} = 0$). The initial populations and coherences in the dressed-state picture will then be given by

$$\tilde{\rho}^{(o)}_{11}(0) = \sin^2\theta \quad , \quad \tilde{\rho}^{(o)}_{22}(0) = \cos^2\theta \quad ,$$

$$\tilde{\rho}^{(o)}_{12}(0) = \tilde{\rho}^{(o)}_{21}(0) = 2\sin\theta\cos\theta \quad ,$$

$$\tan\theta = \frac{2|G|}{\Delta+\Omega_R} \tag{8.15}$$

Note that for the system initially in the ground state, $\tilde{\rho}^{(o)}_{12}(0)$ $\tilde{\rho}^{(o)}_{21}(0)$ are non-zero. In the limit of large detunings, i.e. $|\Delta| >> |G|, \gamma_{21}$, ${}_I\chi^{(1)}_{FWM}(-\delta,t)$ has a simple structure and is given by

$${}_I\chi^{(1)}_{FWM}(-\delta,t) = -2d_{12}^2\left(\frac{G}{\Delta}\right)^2 e^{-i\Omega_R t-\gamma_{21}t/2}\left(\frac{1-e^{-i\delta t}}{-\delta}\right) + O\left(\frac{G}{\Delta}\right)^4 \tag{8.16}$$

The transient four-wave mixing signal is given by

$$S(t) = \left|{}_I\chi^{(1)}_{FWM}(-\delta,t)\right|^2 \propto \frac{4e^{-\gamma_{21}t}}{\Delta^4}\frac{\sin^2\delta t/2}{\delta^2} \quad , \delta=\omega_2-\omega_1 \tag{8.17}$$

Thus Eq.(8.17) clearly shows the existence of a resonance at $\delta(=\omega_2-\omega_1)=0$ which is significant when $\gamma_{21}t \lesssim 1$ but vanishes in the long-time limit. Such a resonance is characterized by a linewidth which has no contribution from relaxation processes but which is essentially determined by the interaction time t. Note that Eq. (8.17) is the same as Eq.(5.8), an expression that we had obtained in Chapter V, using perturbative methods, for the transient FWM signal from a two-level system initially in the ground state.

B. Transient Effects in Optical double Resonance

Consider a cascade-type three-level system [see Fig.5(a)] with levels $|1\rangle$ and $|2\rangle$ spontaneously decaying into levels $|2\rangle$ and $|3\rangle$ respectively at the rates γ_{21} and γ_{32}. The strong (dressing) field ω_1 is near-resonant with the transition $|2\rangle \leftrightarrow |3\rangle$ while the weak field ω_2 is near-resonant with the transition $|1\rangle \leftrightarrow |2\rangle$. The transient effects in such a system have been studied in detail by Mossberg and coworkers.[76] We show how their results can be easily understood in terms of our general result, (8.9)-(8.12). For the above model, the explicit terms of the unperturbed Hamiltonian, and the interactions V and F can be written as

$$H_o = \omega_{13}A_{11}+\omega_{23}A_{22} \tag{8.18}$$

$$V(t) = GA_{23}e^{-i\omega_1 t} + H.c. \quad , \quad G = -\vec{d}_{23}.\vec{e}_1 e^{i\vec{k}_1.\vec{r}} \quad , \tag{8.19}$$

$$F(t) = -d_{12}e_2A_{12}\,e^{-i\omega_2 t} + \text{H.c.}\ ,\ d_{12} = \vec{d}_{12}\cdot\hat{e}_2 e^{i\vec{k}_2\cdot\vec{r}}\ , \qquad (8.20)$$

where the operator A_{ij} stands for $|i\rangle\langle j|$. On making a canonical transformation with

$$U(t) = e^{-i\Omega_\ell t(A_{11}-2A_{22}+A_{33})}\ , \qquad (8.21)$$

we obtain

$$\tilde{h} = (\omega_{13}-\omega_1)A_{11} + \omega_{23}A_{22}+\omega_1 A_{33}\ , \qquad (8.22)$$

$$\tilde{F}(t) = -d_{12}e_2A_{12}e^{-i\delta t} + \text{H.c.}\ ;\ \delta = \omega_2-\omega_1\ . \qquad (8.23)$$

The matrix $\tilde{h}$ can be easily diagonalized with the result

$$\beta_1 = \omega_{13}-\omega_1$$

$$\beta_{2,3} = \omega_1 + \frac{1}{2}(\Delta_1 \pm \Omega_R)\ ,$$

$$\Omega_R = \sqrt{(\Delta_1^2 + 4|G|^2)}\ ,\ \Delta_1 = \omega_{23}-\omega_1\ ,\ G = |G|e^{-i\phi}\ , \qquad (8.24)$$

$$S = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & e^{-i\phi}\sin\theta \\ 0 & e^{i\phi}\sin\theta & \cos\theta \end{bmatrix}\ ,\quad \tan\theta = \frac{2|G|}{\Delta_1+\Omega_R}\ . \qquad (8.25)$$

As in Eq.(7.21), the dressed state $|\beta_i\rangle$ is given by the i^{th} column of the matrix S in (8.25). Making one more canonical transformation with S, we get

$$\tilde{\tilde{F}}(t) = -\tilde{d}^{+} e_2 e^{-i\delta t} + H.c. \quad , \quad (\tilde{d}^{+})^{+} = \tilde{d}^{-} \quad , \tag{8.26}$$

where

$$\tilde{d}^{+} = d_{12}(S^{-1}A_{12}S)$$

$$= d_{12}(\cos\theta|1\rangle\langle 2| - e^{-i\phi}\sin\theta|1\rangle\langle 3|) \tag{8.27}$$

Hence using (8.26) in (7.12), we have

$$\tilde{\tilde{F}}(\Omega) = f_{+}(\Omega)\tilde{d}^{+} + f_{-}(\Omega)\tilde{d}^{-} \equiv \sum_{\alpha}^{-} f_{\alpha}(\Omega)s_{\alpha} \tag{8.28}$$

where

$$f_{+}(\Omega) = 2\pi e_2 \delta(\Omega-\delta)$$

$$f_{-}(\Omega) = 2\pi e_2^{*} \delta(\Omega+\delta) \tag{8.29}$$

The component of the induced polarization in the direction of weak field P(t) will be given by

$$P(t) = Tr(d\rho) = Tr[\tilde{\tilde{d}}(t)\ \tilde{\tilde{\rho}}(t)] \quad ,$$

$$\tilde{\tilde{d}}(t) = \tilde{d}^{-} e^{-i\omega_1 t} + h.c. \equiv \sum_a Q_a e^{-i\omega_a t} \qquad (8.30)$$

The relaxation terms (7.8) can be calculated using (8.25) and these are found to be [see Fig.5(b)]

$$p_{12} = p_{13} = 0 \ ,$$

$$p_{21} = \gamma_{21} \cos^2\theta \ , \ p_{31} = \gamma_{21} \sin^2\theta \ ,$$

$$p_{23} = \gamma_{32} \sin^4\theta \ , \ p_{32} = \gamma_{32} \cos^4\theta$$

$$q_{12} = \frac{1}{2} \left(\gamma_{21} + \gamma_{32} \cos^2\theta \right)$$

$$q_{13} = \frac{1}{2} \left(\gamma_{21} + \gamma_{32} \sin^2\theta \right)$$

$$q_{23} = \frac{1}{2} \gamma_{32} \left(1 + 2\sin^2\theta\cos^2\theta \right) \qquad (8.31)$$

The eigenvalues of the relaxation matrix $\tilde{R}$ are given by

$$\tilde{\lambda}_1 = -\left(p_{21} + p_{31} \right) \ , \ \tilde{\lambda}_2 = -\left(p_{23} + p_{32} \right) \ , \ \tilde{\lambda}_3 = 0 \ . \qquad (8.32)$$

Consider a simple situation where the system could be intitially in the dressed states $|\tilde{2}\rangle$ and/or $|\tilde{3}\rangle$; i.e., $\tilde{\tilde{\rho}}^{(o)}_{11}(0) = 1$, and all off-diagonal elements of $\tilde{\tilde{\rho}}^{(o)}(0)$ are zero. In such a case, the induced polarization describing energy absorption from the probe ω_2 is given by

$$P^{(1)}_{abs}(t) = e^{-i\omega_2 t}\, {}_I\chi^{(1)}_{abs}(\delta,t)\, e_2 + \text{c.c.} \qquad (8.33)$$

where

$$
\begin{aligned}
{}_I\chi^{(1)}_{abs}(\delta,t) = & -\tilde{d}^{-}_{21}\tilde{d}^{+}_{12}\left[a_{23}\left(\frac{1-e^{i(\delta-\tilde{\Lambda}_{12})t}}{\delta-\tilde{\Lambda}_{12}} \right) \right. \\
& \left. + \left[a_{32}\tilde{\tilde{\rho}}^{(o)}_{22}(0) - a_{23}\,\tilde{\tilde{\rho}}^{(o)}_{33}(0) \right] \left(\frac{e^{\tilde{\lambda}_2 t} - e^{i(\delta-\tilde{\Lambda}_{12})t}}{\delta-\tilde{\Lambda}_{12}+i\tilde{\lambda}_2} \right) \right] \\
& - \tilde{d}^{-}_{31}\tilde{d}^{+}_{13}\left[a_{32}\left(\frac{1-e^{i(\delta-\tilde{\Lambda}_{13})t}}{\delta-\tilde{\Lambda}_{13}} \right) \right. \\
& \left. - \left[a_{32}\tilde{\tilde{\rho}}^{(o)}_{22}(0) - a_{23}\,\tilde{\tilde{\rho}}^{(o)}_{33}(0) \right] \left(\frac{e^{\tilde{\lambda}_2 t} - e^{i(\delta-\tilde{\Lambda}_{13})t}}{\delta-\tilde{\Lambda}_{13}+i\tilde{\lambda}_2} \right) \right] ,
\end{aligned}
$$

$$\delta = \omega_2 - \omega_1 , \qquad (8.34)$$

where a_{23} and a_{32} are respectively the steady-state populations of the dressed levels $|\tilde{2}\rangle$ and $|\tilde{3}\rangle$,

$$a_{23} = \frac{p_{23}}{p_{23}+p_{32}} , \qquad a_{32} = \frac{p_{32}}{p_{23}+p_{32}} . \qquad (8.35)$$

The transient absorption spectrum will be related to imaginary part of the time-dependent intensity-dependent susceptibility ${}_I\chi^{(1)}_{abs}(\delta,t)$ [one can show this as in Eqs.(6.31)-(6.33)]. If one assumes that the strong field ω_1 is resonant with the $|2\rangle \leftrightarrow |3\rangle$ transition ($\Delta_1=0$) and that $\gamma_{21} >> \gamma_{32}$, then $q_{12}=q_{13} >> |\tilde{\lambda}_2|$ and the contribution from terms like $e^{i(\delta-\tilde{\Lambda}_{12})t}$ is negligible and hence

can be ignored. In such a case, Eq.(8.34) acquires a very simple structure

$$I^{\chi^{(1)}}_{abs}(\delta,t) = \frac{|d_{12}|^2}{2}\left[\frac{1\mp e^{-\gamma_{32}t/2}}{\Delta_2+|G|-i(\gamma_{21}/2)} + \frac{1\pm e^{-\gamma_{32}t/2}}{\Delta_2-|G|-i(\gamma_{21}/2)}\right],$$

$$\Delta_2 = \omega_2 - \omega_{12} \quad , \qquad (8.36)$$

where ± stands for the two sets of initial conditions (i) $\tilde{\rho}^{(o)}_{22}(0)=1$ and (ii) $\tilde{\rho}^{(o)}_{33}(0) = 1$ respectively. Consider for instance the case when $\tilde{\rho}^{(o)}_{22}(0)=1$. In this case, it is evident from (8.35) that the strength of the peak at $\Delta_2=-|G|$ is $1-e^{-\gamma_{32}t/2}$, while the strength of the peak at $\Delta_2=+|G|$ is $1+e^{-\gamma_{32}t/2}$. Hence at short times, i.e., $\gamma_{32}t \ll 1$, the component at $\Delta_2=-|G|$ is suppressed. However, this component builds up with time and in the long time limit ($\gamma_{32}t \gg 1$) both the components have equal strength. Thus, the equation (8.36) clearly shows the transient suppression of one component of the Autler-Townes doublet, depending on which dressed state the system is initially prepared in. Our analysis yields results in full agreement with the work of Berman et al.[34,76]

Thus, in conclusion, we have developed a formulation of the transient response of a system undergoing arbitrary relaxation and dressed by one or more strong fields. Our theory is valid under arbitrary initial preparation of the system and for all time-scales of interest. An explicit expression for the time-dependent intensity-dependent linear susceptibility is obtained. The existence of the new transient resonances is evident from this expression. The result is specialized to the case of a two-level system interacting with a strong field and a weak field. The various features of the transient resonance are discussed. Our result specialized to the case of a three-level system explains the recently discovered phenomena of the transient suppression of the Autler-Townes doublet when the system is prepared initially in one of the dressed states.

CHAPTER IX

CROSSRELAXATION UNDER STRONG PUMPING CONDITIONS

In Chapter VI, we had examined the nonlinear response of a model four-level system which had two transitions coupled by inelastic collisions. Considering the pump to be weak (treated to second-order in perturbation theory) we studied the effect of crossrelaxation on the saturated absorption and four-wave mixing spectra. For instance, we had shown that crossrelaxation tends to suppress the collision-induced resonant structures, both in the saturated absorption as well as the four-wave mixing spectra. It is of interest to examine how crossrelaxation would affect the response of a system to a probe field in presence of an intense pump field. In the present chapter, we consider the pump to be strong and treat it as a dressing field. Using the methods developed in Chapter VII, we obtain analytical expressions for the intensity-dependent susceptibilities that describe probe absorption and four-wave mixing in the model system of Fig.4. Using these, we examine the effect of crossrelaxation on the probe absorption and four-wave mixing spectra under conditions when the pump is strong. The analytical results clearly show the existence of the line mixing and line narrowing phenomena in the strong-field spectra similar to those in the weak-field spectra discussed in Chapter VI

Consider the four-level system described in Chapter VI (see Fig.4) to be interacting with a strong field ω_ℓ and a weak probe field ω_s. The total field is given by (6.24). The unperturbed Hamiltonian, the strong-field and the weak-field interactions for this model are respectively given by

$$H_o = \frac{\omega_{12}}{2}(A_{11}-A_{22}) + \frac{\omega_{24}}{2}(A_{33}-A_{44}) \quad , \tag{9.1}$$

$$V(t) = G(A_{12}+A_{34})\, e^{-i\omega_\ell t} + H.c., \quad G = -de_\ell \tag{9.2}$$

$$F(t) = -de_s(A_{12}+A_{34})e^{-i\omega_s t} + H.c. \ , \tag{9.3}$$

where A_{ij} stands for the operator $|i\rangle\langle j|$. Note that in (9.2)-(9.3), we have taken $\vec{d}_{12}.\hat{e} = \vec{d}_{34}.\hat{e}=d$ (real). On making the canonical transformations on the basic dynamical equation (7.1) [with H_o,V and F given by Eqs. (9.1)-(9.3) and $L_o\rho=-i[H_o,\rho] + L_D\rho$ given by Eqs. (6.14)] successively with

$$U(t) = e^{-i\omega_\ell(A_{11}-A_{22}+A_{33}-A_{44})t/2} \tag{9.4}$$

and

$$S = \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \ , \quad M_i = \begin{pmatrix} \cos\theta_i & -\sin\theta_i \\ \sin\theta_i & \cos\theta_i \end{pmatrix} \ ,$$

$$\tan\theta_i = \frac{2|G|}{\Delta_i+\Omega_{Ri}} \ ,$$

$$\Omega_{Ri} = \sqrt{(\Delta_i^2 + 4|G|^2)} \quad , \quad i = 1, 2 \quad ,$$

$$\Delta_1 = \omega_{12} - \omega_\ell \quad , \quad \Delta_2 = \omega_{34} - \omega_\ell \quad , \tag{9.5}$$

we obtain the equations of motion in the dressed-atom picture

$$\frac{\partial}{\partial t}\tilde{\tilde{\rho}} = L_o\tilde{\tilde{\rho}} - i[\tilde{\tilde{F}}(t), \tilde{\tilde{\rho}}] \quad , \tag{9.6}$$

$$L_o = -i[\beta,] + L_D \quad , \tag{9.7}$$

where $L_D\tilde{\tilde{\rho}}$ gives the relaxation terms when the dressed-atom approximation is made. Note that in (9.7), β is the unperturbed Hamiltonian of the dressed system

$$\beta = \sum_i \beta_i |i\rangle\langle i| \quad , \quad i = 1, 2, 3, 4,$$

$$\beta_{1,2} = \pm \frac{1}{2} \Omega_{R1} \quad , \quad \beta_{3,4} = \pm \frac{1}{2} \Omega_{R2} \tag{9.8}$$

Thus the β_i, i=1,2,3,4 in (9.8) are the energies of the dressed system while the eigenstates $|\beta_i\rangle$ of β are given by the i^{th} column of the matrix S defined in (9.5). The operator $L_o\tilde{\tilde{\rho}}$ (9.7) is explicitly given

by

$$\begin{bmatrix} (L_o\tilde{\tilde{\rho}})_{12} \\ (L_o\tilde{\tilde{\rho}})_{34} \end{bmatrix} = \tilde{M} \begin{bmatrix} \tilde{\tilde{\rho}}_{12} \\ \tilde{\tilde{\rho}}_{34} \end{bmatrix} \quad , \quad \begin{bmatrix} (L_o\tilde{\tilde{\rho}})_{21} \\ (L_o\tilde{\tilde{\rho}})_{43} \end{bmatrix} = \tilde{M}^* \begin{bmatrix} \tilde{\tilde{\rho}}_{21} \\ \tilde{\tilde{\rho}}_{43} \end{bmatrix} \quad ,$$

$$\tilde{M} = \begin{pmatrix} -i\tilde{\Lambda}_{12} & \tilde{\xi} \\ \tilde{\xi} & -i\tilde{\Lambda}_{34} \end{pmatrix}$$

$$\tilde{\Lambda}_{12} = \Omega_{R1} - iq_{12} \quad , \quad \tilde{\Lambda}_{34} = \Omega_{R2} - iq_{34} \tag{9.9}$$

and

$$(L_o\tilde{\rho})_{ll} = \sum_{k}^{-} (p_{lk}\tilde{\rho}_{kk} - p_{kl}\tilde{\rho}_{ll}) \; , \quad l=1,2,3,4 \; . \tag{9.10}$$

The various relaxation parameters can be calculated by using (9.5) in (7.8) and these are given by

$$p_{12} = 2\gamma \sin^4\theta_1 \quad , \quad p_{21} = 2\gamma \cos^4\theta_1 \quad ,$$

$$p_{34} = 2\gamma \sin^4\theta_2 \quad , \quad p_{43} = 2\gamma \cos^4\theta_2 \quad ,$$

$$p_{13} = p_{31} = p_{24} = p_{42} = \sigma a + \xi c \equiv \gamma_1 \quad ,$$

$$p_{14} = p_{41} = p_{23} = p_{32} = \sigma b - \xi c \equiv \gamma_2 \quad ,$$

$$\tilde{\xi} = \sigma c + \xi a \quad ,$$

$$q_{12} = \sigma + \gamma(1+2\sin^2\theta_1\cos^2\theta_1)$$

$$q_{34} = \sigma + \gamma(1+2\sin^2\theta_2\cos^2\theta_2) \quad , \tag{9.11}$$

where we have defined a,b and c as

$$a = \sin^2\theta_1\sin^2\theta_2 + \cos^2\theta_1\cos^2\theta_2$$

$$b = \sin^2\theta_1\cos^2\theta_2 + \cos^2\theta_1\sin^2\theta_2$$

$$c = \frac{1}{2}\sin 2\theta_1 \sin 2\theta_2 \qquad (9.12)$$

Note that σ is the rate of inelastic collisions and ξ is the cross-relaxation parameter. The parameter $\tilde{\xi}$ couples the coherences $\tilde{\rho}_{12}$ and $\tilde{\rho}_{34}$ in the dressed-atom picture. Note that this coupling is important since the factor $\tilde{\xi}/|\Omega_{R1}-\Omega_{R2}|$ is quite significant and it cannot be thrown away in the dressed-atom approximation. The steady-state level populations of the dressed system are given by

$$\tilde{\rho}_{11}^{(o)} = \kappa[2\gamma_1\gamma_2 + \gamma_1 p_{34} + \gamma_2 p_{43} + p_{12}(\sigma+p_{34}+p_{43})] \ ,$$

$$\tilde{\rho}_{22}^{(o)} = \kappa[2\gamma_1\gamma_2 + \gamma_1 p_{34} + \gamma_2 p_{43} + p_{21}(\sigma+p_{34}+p_{43})] \ , \qquad (9.13)$$

and $\tilde{\rho}_{33}^{(o)}$ and $\tilde{\rho}_{44}^{(o)}$ are determined from (9.13) by interchanging $p_{12} \leftrightarrow p_{34}$, $p_{21} \leftrightarrow p_{43}$ in the expressions for $\tilde{\rho}_{11}^{(o)}$ and $\tilde{\rho}_{22}^{(o)}$ respectively. The normalization constant κ is easily determined by requiring that $\mathrm{Tr}\ \tilde{\tilde{\rho}}^{(o)}=1$. The operator $\tilde{\tilde{F}}(t)$ in (9.6) which represents the interaction of the dressed system with the weak field is given by

$$\tilde{\tilde{F}}(t) = -\tilde{d}^{+} e_s \, e^{-i\Omega t} + \text{H. c.}$$

$$(\tilde{d}^{+})^{+} = \tilde{d}^{-} \ , \qquad \Omega = \omega_s - \omega_\ell \ , \qquad (9.14)$$

where

$$\tilde{d}^{+} = dS^{-1}(A_{12}+A_{34})S$$

$$= d\left\{ -\sin\theta_1\cos\theta_1(|1\rangle\langle 1| - |2\rangle\langle 2|) + \cos^2\theta_1|1\rangle\langle 2| \right.$$

$$\left. - \sin^2\theta_1|2\rangle\langle 1| + |1\rangle \leftrightarrow |3\rangle \ , \ |2\rangle \leftrightarrow |4\rangle \ , \ \theta_1 \leftrightarrow \theta_2 \right\} \tag{9.15}$$

The induced polarization is given by

$$P(t) = \left\{ d\rho(t) \right\} = \left\{ \tilde{\tilde{d}}(t)\ \tilde{\rho}(t) \right\} \tag{9.16}$$

where

$$\tilde{\tilde{d}}(t) = \tilde{d}^{-}e^{-i\omega_1 t} + \tilde{d}^{+}e^{i\omega_1 t} = \sum_a Q_a e^{-i\omega_a t} \tag{9.17}$$

The induced polarization to first order in the weak field and to all orders in the strong (dressing) field can be expressed as

$$P^{(1)}(t) = e^{-i(\omega_1+\Omega)t}\ {}_I\chi^{(1)}_{abs}(\Omega) + e^{-i(\omega_1-\Omega)t}\ {}_I\chi^{(1)}_{FWM}(-\Omega) + c.c. \tag{9.18}$$

where ${}_I\chi^{(1)}_{abs}(\Omega)$ and ${}_I\chi^{(1)}_{FWM}(-\Omega)$ are respectively the intensity-dependent susceptibilities that describe probe absorption and four-wave mixing. These intensity-dependent susceptibilities can be obtained from the bare-atom result (6.28) by the usual renormalization procedure which in the present case consists of letting $d^{\mu}\rightarrow Q_a$, $d^{\alpha}\rightarrow s_{\alpha}$, $\xi \rightarrow \tilde{\xi}$, and using the translation table (7.16). In what follows, we use the analytical expressions for these inten-

sity-dependent susceptibilities to examine the effect of crossrelaxation on the probe absorption and four-wave mixing spectra of the model system of Fig.4.

A. Effect of crossrelaxation on probe absorption in presence of a strong pump

We have shown that the intensity-dependent susceptibility $I\chi^{(1)}_{abs}(\Omega)$ that describes energy absorption from probe ω_2 in presence of the strong pump ω_1 is given by expression

$$I\chi^{(1)}_{abs}(\Omega) = d^2\Big[\frac{A_+}{(\Omega-\Omega_2+\eta)+i(q_{34}-\kappa)} + \frac{A_-}{(\Omega-\Omega_1-\eta)+i(q_{12}+\kappa)} - \frac{B_+}{(\Omega+\Omega_2-\eta)+i(q_{34}-\kappa)} - \frac{B_-}{(\Omega+\Omega_1+\eta)+i(q_{12}+\kappa)}\Big] , \quad (9.20)$$

where

$$A_\pm = \big(\tilde\rho^{(o)}_{11}-\tilde\rho^{(o)}_{22}\big)\cos^2\theta_1\big(\cos^2\theta_1\tilde a_\mp \pm \cos^2\theta_2\tilde b\big) + \big(\tilde\rho^{(o)}_{33}-\tilde\rho^{(o)}_{44}\big)\cos^2\theta_2\big(\cos^2\theta_2\tilde a_\pm \pm \cos^2\theta_1\tilde b\big) ,$$

$$B_\pm = \big(\tilde\rho^{(o)}_{11}-\tilde\rho^{(o)}_{22}\big)\sin^2\theta_1\big(\sin^2\theta_1\tilde a_\mp \pm \sin^2\theta_2\tilde b^*\big) + \big(\tilde\rho^{(o)}_{33}-\tilde\rho^{(o)}_{44}\big)\sin^2\theta_2\big(\sin^2\theta_2\tilde a^*_\pm \pm \sin^2\theta_1\tilde b^*\big) , \quad (9.21)$$

$$\tilde a_\pm = \frac{1}{2}\Big(1 \pm \frac{i\tilde\beta}{\sqrt{(\tilde\xi^2-\tilde\beta^2)}}\Big) , \qquad \tilde b = \frac{\tilde\xi}{2\sqrt{(\tilde\xi^2-\tilde\beta^2)}} ,$$

$$\tilde{\beta} = \frac{1}{2} (\tilde{\Lambda}_{12} - \tilde{\Lambda}_{34})$$

In the expression (9.20), κ and η are respectively the real and imaginary parts of the quantity

$$z = i\left(\sqrt{(\tilde{\beta}^2-\tilde{\xi}^2)} - \beta\right) \equiv \kappa + i\eta \qquad (9.23)$$

Note that z is zero in the absence of collisions. The expression (9.20) has a simple structure in the absence of collisions ($\sigma = \xi = 0$).

$$I\chi^{(1)}_{abs}(\Omega) = d^2 \left\{ \left(\tilde{\rho}^{(o)}_{11} - \tilde{\rho}^{(o)}_{22} \right) \left(\frac{\cos^4\theta_1}{\Omega-\Omega_{R1}+iq_{12}} - \frac{\sin^4\theta_1}{\Omega+\Omega_{R1}+iq_{12}} \right) \right.$$

$$\left. + \left(\tilde{\rho}^{(o)}_{33} - \tilde{\rho}^{(o)}_{44} \right) \left(\frac{\cos^4\theta_2}{\Omega-\Omega_{R2}+iq_{34}} - \frac{\sin^4\theta_2}{\Omega+\Omega_{R2}+iq_{34}} \right) \right\} . \qquad (9.24)$$

Hence in absence of collisions, the probe absorption spectrum contains resonances at

$$\Omega = -\Omega_{R2}, \; -\Omega_{R1}, \; \Omega_{R1}, \; \Omega_{R2} \qquad (9.25)$$

characterized by widths q_{34}, q_{12}, q_{12} and q_{34} respectively. The weights as well as the widths of these resonances depend on the detunings Δ_1, Δ_2 and the strength of the pump G. However when collisions are present, it can be seen from (9.20) that the probe absorption spectrum will in general exhibit resonances at

$$\Omega = -(\Omega_{R2} - \eta) \ , \ -(\Omega_{R1} + \eta) \ , \ \Omega_{R1} + \eta \ , \ \Omega_{R2} - \eta \ , \qquad (9.26)$$

which are respectively characterized by widths $|q_{34}-\kappa|$, $|q_{12}+\kappa|$, $|q_{12}+\kappa|$ and $|q_{34}-\kappa|$. The quantities η and κ are thus the collision-induced contributions respectively to the shifts and widths of the resonances in (9.25). The weights of the resonances in (9.26) are determined by the quantities $A_{\pm}$ and $B_{\pm}$ (9.21) and these depend on the collisional and the pump parameters in a complicated way. The general expression (9.20) already shows the mixing and narrowing of the various lines which arises due to collisions. For instance if κ and η are both positive, then the lines at Ω_{R1} and Ω_{R2} [or at $-\Omega_{R1}$ and $-\Omega_{R2}$] are shifted closer to each other by an amount 2η and further, one of the lines has a narrower width than the other if $|q_{34}-\eta| < |q_{12}+\eta|$. This is the usual mixing and narrowing phenomena which we had discussed in detail in Chapter VI in the case when the pump was absent, or when it was weak. Hence it is evident from the expression (9.20) that such mixing and narrowing phenomena occur in the probe absorption spectrum even when the pump is intense. In the following we examine a few special situations where the result (9.20) has a simple structure. Consider the case when the pump is tuned to the center of the two transitions, i.e., $\Delta_1=-\delta$, $\Delta_2=+\delta$. In this case, Eq. (9.20) reduces to

$$I\chi^{(1)}_{abs}(\Omega) = \frac{d^2}{2}\left[\tilde{\rho}^{(0)}_{11} - \tilde{\rho}^{(0)}_{22}\right]\frac{\delta}{\sqrt{(\delta^2+G^2)}}\left\{\frac{1}{\Omega-\Omega_{R2}+i\Gamma_-} + \frac{1}{\Omega-\Omega_{R1}+i\Gamma_+}\right.$$

$$\left. + \frac{1}{\Omega+\Omega_{R2}+i\Gamma_-} + \frac{1}{\Omega+\Omega_{R1}+i\Gamma_+}\right\} \ , \qquad (9.27)$$

where

$$\Gamma_{\pm} = \sigma + \gamma \left(1 + \frac{2G^2}{(\delta^2+4G^2)} \right) \pm \left(\frac{\sigma+\xi}{2} \right) \frac{4G^2}{\delta^2+4G^2} \quad . \quad (9.28)$$

Note that in the case when $\Delta_1 = -\delta$, $\Delta_2 = \delta$, the mixing parameter η is zero. Hence the probe absorption spectrum in this case has resonances as in (9.25). However, some of these resonances can be narrower than the others. For instance the resonances at $\Omega=\pm\Omega_{R2}$ have a narrower width Γ_- (9.28). Note that here both the inelastic collision rate σ as well as the crossrelaxation ξ contribute to the narrowing of the lines, unlike in the linear absorption spectrum in the absence of pump where only the crossrelaxation ξ contributed to the narrowing. In the case when $\xi \sim \sigma$ and $\frac{\delta}{G} << 1$, the resonances at $\Omega=\pm\Omega_{R2}$ have a width $\Gamma_- \sim 3\gamma/2$ which is independent of the collisional parameters σ and ξ. Another situation of interest is when the pump is tuned to one of the transitions, for example, the $|1\rangle \leftrightarrow |2\rangle$ transition so that $\Delta_1=0$. In the case when $\Delta_1=0$ and $\frac{\delta}{G} << 1$, the expression (9.20) reduces to

$$I^{\chi^{(1)}}_{abs}(\Omega) = d^2 \left\{ \frac{A_+}{\Omega-2G-\frac{\delta^2}{2G}+i\Gamma_-} + \frac{A_-}{\Omega-2G-\frac{\delta^2}{2G}+i\Gamma_+} - \frac{B_+}{\Omega+2G+\frac{\delta^2}{2G}+i\Gamma_-} \right.$$

$$\left. - \frac{B_-}{\Omega+2G+\frac{\delta^2}{2G}+i\Gamma_+} \right\} \quad , \quad (9.29)$$

where

$$A_{\pm} = \frac{1}{2} \left(\tilde{\rho}^{(o)}_{33} - \tilde{\rho}^{(o)}_{44} \right) \left[1 \pm \frac{1}{4} + \frac{\delta^2}{2G^2} \left(1 \pm \frac{i(2G+i\gamma)-(3\sigma+\xi)}{\sigma+\xi} \right) \right] \quad .$$

$$B_{\pm} = \pm \frac{1}{4}\left[\tilde{\rho}_{33}^{(o)} - \tilde{\rho}_{44}^{(o)}\right] \frac{\delta^2}{4G^2} \quad , \tag{9.30}$$

and the widths Γ_+ and Γ_- are now given by

$$\Gamma_+ = \frac{3\gamma}{2} - \frac{\gamma\delta^2}{4G^2} + \frac{3\sigma+\xi}{2} - \frac{\sigma\delta^2}{4G^2} \quad ,$$

$$\Gamma_- = \frac{3\gamma}{2} - \frac{\gamma\delta^2}{4G^2} + \frac{\sigma-\xi}{2} + \frac{\sigma\delta^2}{4G^2} \quad . \tag{9.31}$$

Thus one can see from Eqs. (9.29)-(9.30) that the probe absorption spectrum in the limit $\Delta_1=0$, $\frac{\delta}{G} << 1$, consists of a doublet at $\Omega = 2G + \frac{\delta^2}{2G}$ and $\Omega = -2G - \frac{\delta^2}{2G}$ with a width given by Γ_-. However the strength of the peak at $\Omega=-2G-\delta^2/2G$ is quite small compared to that of the peak at $\Omega=2G+\delta^2/2G$ since $|B_{\pm}|<<|A_{\pm}|$ (9.30). The effect of the other Lorentzian terms with Γ_+ in (9.29) is merely to reduce the strength of the two lines.

B. Effect of crossrelaxation on the four-wave mixing signal in presence of a strong pump

We have shown that the intensity-dependent susceptibility. $I\chi^{(1)}_{FWM}(-\Omega)$ that describes four-wave mixing in the model system of Fig.4 is given by

$$I\chi^{(1)}_{FWM}(-\Omega) = d^2\left[\frac{C_+}{(-\Omega-\Omega_{R2}+\eta)+i(q_{34}-\kappa)} + \frac{C_-}{(-\Omega-\Omega_{R1}-\eta)+i(q_{12}+\kappa)}\right.$$

$$\left. - \frac{D_+}{(-\Omega+\Omega_{R2}-\eta)+i(q_{34}-\kappa)} - \frac{D_-}{(-\Omega+\Omega_{R1}+\eta)+i(q_{12}+\kappa)}\right], \tag{9.32}$$

where

$$C_{\pm} = -\left[\tilde{\rho}^{(o)}_{11} - \tilde{\rho}^{(o)}_{22}\right] \sin^2\theta_1 \left[\sin^2\theta_1 \tilde{a}_{\mp} \pm \cos^2\theta_2 \tilde{b}\right]$$

$$- \left[\tilde{\rho}^{(o)}_{33} - \tilde{\rho}^{(o)}_{44}\right] \sin^2\theta_2 \left[\cos^2\theta_2 \tilde{a}_{\pm} \pm \cos^2\theta_1 \tilde{b}\right] \quad ,$$

$$D_{\pm} = -\left[\tilde{\rho}^{(o)}_{11} - \tilde{\rho}^{(o)}_{22}\right] \cos^2\theta_1 \left[\sin^2\theta_1 \tilde{a}^{*}_{\mp} \pm \sin^2\theta_2 \tilde{b}^{*}\right]$$

$$- \left[\tilde{\rho}^{(o)}_{33} - \tilde{\rho}^{(o)}_{44}\right] \cos^2\theta_2 \left[\sin^2\theta_2 \tilde{a}^{*}_{\pm} \pm \sin^2\theta_2 \tilde{b}^{*}\right] \quad . \qquad (9.33)$$

Here the quantities $\tilde{a}_{\perp}$, $\tilde{b}_{\pm}$ are as given by Eq.(9.22). Note that the expression in (9.32) has the same structure as that in (9.20) except for the fact that Ω is now replaced by $-\Omega$, and $A_{\pm}, B_{\pm}$ are respectively replaced by $C_{\pm}$ and $D_{\pm}$. Hence the resonances in the four-wave mixing spectrum occur at the same frequencies [as in (9.26)] as in the probe absorption spectrum. Thus, the resonances in the four-wave mixing spectrum are at

$$-\Omega = -(\Omega_{R2}-\eta),\ -(\Omega_{R1}+\eta),\ \Omega_{R1}+\eta,\ \Omega_{R2}-\eta \quad , \qquad (9.34)$$

which are respectively characterized by widths $|q_{34}-\kappa|$, $|q_{12}+\kappa|$, $|q_{12}+\kappa|$ and $|q_{12}-\kappa|$. In the absence of collisions, the expression in (9.32) reduces to

$$I\chi^{(1)}_{FWM}(-\Omega) = d^2 \left\{ \left(\tilde{\rho}^{(o)}_{11} - \tilde{\rho}^{(o)}_{22} \right) \left[\frac{\sin^2\theta_1 \cos^2\theta_1}{\Omega+\Omega_{R1}-i\gamma_{12}} - \frac{\sin^2\theta_1 \cos^2\theta_1}{\Omega-\Omega_{R1}-i\gamma_{12}} \right] \right.$$

$$\left. + \left(\tilde{\rho}^{(o)}_{33} - \tilde{\rho}^{(o)}_{44} \right) \left[\frac{\sin^2\theta_2 \cos^2\theta_2}{\Omega+\Omega_{R2}-i\gamma_{34}} - \frac{\sin^2\theta_2 \cos^2\theta_2}{\Omega-\Omega_{R2}-i\gamma_{34}} \right] \right\} . \qquad (9.35)$$

Thus the four-wave mixing spectrum in the absence of collisions consists of four resonances, namely at $\Omega=\pm\Omega_{R1}$, and $\Omega=\pm\Omega_{R2}$. However, when collisions are present, the mixing and narrowing phenomena occur due to the presence of the collision-induced intensity-dependent parameters η and κ in the expression (9.32). In the case when the pump is tuned to the center of the two transitions, i.e., $\Delta_1 = -\delta$, $\Delta_2 = \delta$, the quantities $C_\pm$ and $D_\pm$ in Eq. (9.32) become zero. Hence the four-wave mixing spectrum in this case vanishes. Note that this is so because in deriving (9.32) we have made the dressed-atom approximation. However the non-secular terms which have been thrown away under the dressed-atom approximation give rise to nonvanishing contribution to the four-wave mixing spectrum. In the other situation where the pump is resonant with one of the transitions, namely the $|1\rangle \leftrightarrow |2\rangle$ transition, and in the limit $\frac{\delta}{G} << 1$, the expression in (9.32) reduces to

$$I\chi^{(1)}_{FWM}(-\Omega) = d^2 \left[\frac{C_+}{-\Omega-2G-\frac{\delta^2}{2G}+i\Gamma_-} - \frac{D_+}{-\Omega+2G+\frac{\delta^2}{2G}+i\Gamma_-} - \right.$$

$$\left. - \frac{D_-}{-\Omega+2G+\frac{\delta^2}{2G}+i\Gamma_+} \right] , \qquad (9.36)$$

where

$$C_+ = -\left(\tilde{\rho}_{33}^{(o)} - \tilde{\rho}_{44}^{(o)}\right)\frac{\delta^2}{4G^2} \quad ,$$

$$D_\pm = -\left(\tilde{\rho}_{33}^{(o)} - \tilde{\rho}_{44}^{(o)}\right)\left[\pm\frac{1}{4} + \frac{\delta^2}{8G^2}\left(1 \mp \frac{3\sigma+\xi}{2(\sigma+\xi)}\right)\right], \qquad (9.37)$$

and the widths Γ_+ and Γ_- are given by

$$\Gamma_+ = \frac{3\gamma}{2} - \frac{\gamma\delta^2}{4G^2} + \frac{3\sigma+\xi}{2} - \frac{\sigma\delta^2}{4G^2} \quad ,$$

$$\Gamma_- = \frac{3\gamma}{2} - \frac{\gamma\delta^2}{4G^2} + \frac{\sigma-\xi}{2} + \frac{\sigma\delta^2}{4G^2} \qquad (9.38)$$

Thus in this limit, the four-wave mixing spectrum consists of two lines at $\Omega=\pm(2G+\frac{\delta^2}{2G})$ characterized by a width Γ_-. However since $|C_+|<<|D_+|$, the line at $\Omega=-(2G+\delta^2/2G)$ is expected to be weak compared to the line at $\Omega=+(2G+\delta^2/2G)$. The effect of the other Lorentzian at $\Omega=+(2G+\frac{\delta^2}{2G})$ with the much broader width Γ_+ is merely to reduce the strength of the line at $\Omega=+(2G+\frac{\delta^2}{2G})$.

Thus, in conclusion, we have studied the effect of cross-relaxation on probe absorption and four-wave mixing under conditions when the pump is strong. Analytical expressions for the intensity-dependent susceptibilities describing probe absorption and four-wave mixing are obtained. These analytical expressions enable us to obtain a qualitative understanding of the effect of crossrelaxation on the probe absorption and the four-wave mixing

spectra. Various special cases are discussed. It is evident from the structure of these expressions that crossrelaxation enhances the line mixing and the line narrowing effects in the strong-field spectra.

CHAPTER X

EFFECTS OF ARBITRARY RELAXATION ON TWO-TIME CORRELATION FUNCTIONS

In the foregoing chapters, we have developed a formulation of nonlinear response theory in terms of the nonlinear susceptibilities, which are related to the mean value of the induced polarization. As we have shown in the previous chapters, the nonlinear susceptibilities are capable of describing a wide variety of nonlinear optical phenomena such as probe absorption, four-wave mixing, etc. However, there are situations where a knowledge of the mean value of the induced polarization is not enough. In phenomena like resonance fluorescence[21] and squeezing,[22] the quantum mechanical fluctuations in the generated fields are important. Such fluctuations in general are determined in terms of the two-time and other multitime correlation functions of the electric field operator.[23] Since it is the induced dipole moment that drives the generated fields, the correlation functions of the electric field operator are in turn related to the correlation functions of the dipole moment operator, as a consequence of Eq. (1.2). For example, the resonance fluorescence spectrum is related to the two-time correlation function $\langle E^-(t)E^+(t')\rangle$ of the electric field operator, which in turn is related to the two-time correlation function $\langle p^-(t)p^+(t')\rangle$ of the dipole moment operator, where E^+ and E^- [p^+ and p^-] are respectively the positive and negative frequency parts of the electric field operator [dipole moment operator]. Similarly, in phenomena like squeezing[22,77] and

antibunching,[78,79] the two-time correlation function $\langle E^+(t)E^+(t')\rangle$ (referred to as the anomalous correlator[24,80]) is important. In particular, the spectrum of squeezing is determined by such anomalous correlation functions. The correlation function $\langle E^+(t)E^+(t')\rangle$ will be related to the correlation function $\langle p^+(t)p^+((t')\rangle$ of the dipole moment operator. The non-factorizability of correlation functions like $\langle p^-(t)p^+(t')\rangle$ [i.e., $\langle p^-(t)p^+(t')\rangle \neq \langle p^-(t)\rangle\langle p^+(t')\rangle$] is due to the presence of fluctuations about the mean value of the induced polarization. The fluctuations in the induced polarization arise due to the stochastic nature of the interaction between the atom and its environment. In an atomic vapor for instance, the fluctuations arise due to the collisions and spontaneous emission. The fluctuations that arise due to the collisions for instance give rise to a redistributed component[25] in the resonance fluorescence spectrum of a two-level atom in presence of a weak field. The effects of relaxation on the two-time correlation functions of the dipole moment operator will also show themselves up in the two-time correlation functions of the electric field operator. Thus we can study the effect of relaxation on the quantum mechanical properties of the generated fields such as squeezing and antibunching.

In this chapter we develop a theory which will enable us to study the effects of arbitrary relaxation on the two-time correlation functions of a system that is interacting with fields, some of which may be strong. In Section II we give a Liouville operator formulation of the two-time correlation functions of the physical

observables of a system that is interacting with a reservoir and with external fields. Here we make use of the quantum regression theorem[81,82] which is valid when the correlation time of the reservoir is much smaller than the typical relaxation times of the system. We give explicit expressions for the two-time correlation functions of the dipole moment operator to second order in the external fields. In Section III we investigate the effect of collisions on the fluorescence spectrum and the anomalous correlator of a two-level atom. In Section IV, we show how the two-time correlation functions in presence of a strong field can be obtained by using the dressed-atom approach developed in Chapter VII. We also give explicit results for the correlation functions of a two-level atom dressed by a strong field.

II. LIOUVILLE OPERATOR FORMULATION OF THE TWO-TIME CORRELATION FUNCTIONS

Consider a quantum mechanical system that is interacting with a reservoir and with external fields. The dynamics of the atom-field interaction is described by the equation of motion

$$\frac{\partial \rho}{\partial t} = L_o \rho + L_f(t)\, \rho \quad , \tag{10.1}$$

where L_o [Eq.(2.2)] and $L_f(t) = -i[H_f(t), \ ]$ respectively describe the effects of relaxation and the interaction with the external fields. It follows from Eq.(10.1) that the density operator at time $t + \tau$ ($\tau > 0$) can be expressed in terms of the density

operator at an earlier time t as follows:

$$\rho(t+\tau) = S(t+\tau, t)\ \rho(t) \quad , \tag{10.2}$$

where

$$S(t+\tau,t) = e^{L_o t}\left[\ T \exp \int_t^{t+\tau} dt'\ e^{-L_o t'}\ L_f(t')\ e^{L_o t'}\ \right] e^{-L_o t} \quad , \tag{10.3}$$

is the time evolution operator and T in (10.3) stands for the chronological time-ordering operator. We can express S in the form

$$S(t+\tau, t) = \sum_{k=o}^{\infty} S^{(k)}(t+\tau,t) \quad , \tag{10.4}$$

where

$$S^{(o)}(t+\tau, t) = e^{L_o \tau} \quad ,$$

$$S^{(k)}(t+\tau,t) = \int_o^{\tau} dt_1 \ldots \int_o^{t_{k-1}} dt_k\ e^{L_o(t+\tau-t_1)}\ L_f(t+t_1)\ e^{L_o(t_1-t_2)}$$

$$\times\ L_f(t+t_2)\ldots e^{L_o(t_{n-1}-t_n)}\ L_f(t+t_n)\ e^{L_o(t_n-t)} \quad ,$$

$$k = 1, 2, \ldots, \tag{10.5}$$

The expectation value of a physical observable A can be expressed in terms of (10.2) as

$$\langle A(t+\tau)\rangle = \mathrm{Tr}[A\ S(t+\tau,t)\ \rho(t)] \tag{10.6}$$

Now the quantum regression theorem[81,82] can be used to obtain the two-time correlation function of physical observables A and B as follows.

$$\langle A(t+\tau)B(t)\rangle = Tr[A\ S(t+\tau,t)B\ \rho(t)] \qquad (10.7)$$

Similarly, we have

$$\langle B(t)\ A(t+\tau)\rangle = Tr[A\ S(t+\tau,t)\ \rho(t)\ B] \quad . \qquad (10.8)$$

Note that Eqs.(10.7) and (10.8) are valid to all orders in the interaction with the external fields. However, in many cases, the applied fields are weak and hence can be treated perturbatively. The correlation functions to n^{th} order in the external fields can be obtained from Eq.(10.7)-(10.8) on using Eqs.(10.4)-(10.5). We have

$$\langle A(t+\tau)B(t)\rangle^{(n)} = \sum_{k=o}^{n} Tr\left\{ A\ S^{(k)}(t+\tau,t)B\rho^{(n-k)}(t) \right\} \quad , \qquad (10.9)$$

$$\langle B(t)A(t+\tau)\rangle^{(n)} = \sum_{k=o}^{n} Tr\left\{ A\ S^{(k)}(t+\tau,t)\ \rho^{(n-k)}(t)\ B \right\} \quad , \qquad (10.10)$$

where $S^{(k)}$ is given by Eq.(10.5). The expressions (10.9) and (10.10) can be simplified if one writes $S^{(k)}$ in the form

$$S^{(k)}(t+\tau,t) = \int_0^{\tau} dt_1 \int_0^{\tau-t_1} dt_2 \ldots \int_0^{\tau-\sum_{i=1}^{k-1} t_i} dt_k \; e^{L_o t_1}$$

$$\times \; L_f(t+\tau-t_1)\, e^{L_o t_2} \ldots\ldots\, e^{L_o t_n}\, L_f(t+\tau-\sum_{i=1}^{k} t_i)$$

$$\times \; e^{L_o(t+\tau-\sum_{i=1}^{k} t_i)} \; . \qquad (10.11)$$

Note that (10.11) is obtained by making a series of transformations $t_1 \rightarrow \tau - t_1$, $t_2 \rightarrow \tau - t_1 - t_2, \ldots, t_k \rightarrow \tau - \sum_{i=1}^{k} t_i$ in (10.5), as in (3.4)-(3.6). On using the Fourier transform of $H_f(t)$, $L_f(t)$ [Eq.(2..21)] and using the convolution theorem for Laplace transforms, $S^{(k)}(t+\tau,t)$ acquires a much simpler form

$$S^{(k)}(t+\tau,t) = \left(\frac{i}{2\pi}\right) \int_{-\infty}^{\infty} d\omega_1 \ldots \int_{-\infty}^{\infty} d\omega_k \; e^{-i(t+\tau)\sum_{i=1}^{k}\omega_i}$$

$$\times \; \underset{kl}{\text{sym}} \left(\frac{1}{2\pi i}\right) \int_{\varepsilon-i\infty}^{\varepsilon+i\infty} dz \; e^{z\tau}\, (iz' + \sum_{i=1}^{k} \omega_i - iL_o)^{-1}\, L_f(\omega_1)$$

$$\times \; (iz' + \sum_{i=2}^{k} \omega_i - iL_o)^{-1}\, L_f(\omega_2) \ldots L_f(\omega_k)\, (iz'-iL_o)^{-1} \; ,$$

$$z' = z + i\sum_{i=1}^{k} \omega_i \; . \qquad (10.12)$$

The symbol 'sym' in Eq.(10.12) has the usual meaning as in Eq.(2.26) and it implies that the expression on the right-hand side has to be symmetrized with respect to the indices ω_i, α_i. Hence now we can use (10.9), (10.12) to obtain the dipole-dipole correlation function $\langle p_\mu(t+\tau)p_\nu(t)\rangle^{(n)}$. For this purpose we let $A \rightarrow d^\mu$, $B \rightarrow d^\nu$ in (10.9) and write

$$L_f(\omega) = -\sum_{\alpha} L_\alpha E_\alpha(\omega) , \quad L_\alpha = -i[d^\alpha ,] \tag{10.13}$$

in (10.12). The Laplace transform of the correlation function $\langle p_\mu(t+\tau)p_\nu(t)\rangle^{(n)}$ is then given by

$$\hat{f}^{(n)}_{\mu\nu}(z,t) = \int_0^\infty dz\, e^{z\tau} \langle p_\mu(t+\tau)p_\nu(t)\rangle^{(n)}$$

$$= iTr\left[d^\mu (iz - iL_o)^{-1} d^\nu \rho^{(n)}(t) \right]$$

$$- \sum_{k=1}^{n} \left(\frac{1}{2\pi} \right)^k \frac{sym}{k!} \int_0^\infty d\omega_1 \ldots \int_\infty^\infty d\omega_k\, e^{-it\sum_{i=1}^{k}\omega_i} E_{\alpha_1}(\omega_1)$$

$$\ldots E_{\alpha_k}(\omega_k)\,(-1)^{k+1}\, Tr\left[d^\mu \left(iz' + \sum_{i=1}^{k}\omega_i - iL_o\right)^{-1} L_{\alpha_1}\right.$$

$$\left. \times \left(iz' + \sum_{i=2}^{k}\omega_i - iL_o\right)^{-1} L_{\alpha_2} \ldots L_{\alpha_k} (iz' - iL_o)^{-1} d^\nu \rho^{(n-k)}(t) \right] ,$$

$$z' = z + i\sum_{i=1}^{k}\omega_i . \tag{10.14}$$

A similar expression can be written down for the Laplace transform of the correlation function $\langle p_\nu(t)p_\mu(t+\tau)\rangle^{(n)}$ simply by replacing $d^\nu\rho^{(n)}(t)$ and $d^\nu\rho^{(n-k)}(t)$ in (10.14) by $\rho^{(n)}(t)d^\nu$ and $\rho^{(n-k)}(t)d^\nu$ respectively. Thus we have

$$\hat{g}^{(n)}_{\mu\nu}(z,t) = \int_0^\infty dz\, e^{-z\tau} \langle p_\nu(t)\, p_\mu(t+\tau)\rangle^{(n)}$$

$$= \hat{f}_{\mu\nu}(z,t)\Big|_{d^\nu\rho^{(n-k)}(t) \to \rho^{(n-k)}(t)d^\nu} , \quad k=0,1,2,\ldots$$

(10.15)

Note that the steady-state correlation functions $\langle p_\mu(\tau)p_\nu(o)\rangle^{(n)} = \lim_{t\to\infty} \langle p_\mu(t+\tau)p_\nu(t)\rangle^{(n)}$ and $\langle p_\nu(o)p_\mu(\tau)\rangle^{(n)} = \lim_{t\to\infty} \langle p_\nu(t)p_\mu(t+\tau)\rangle^{(n)}$ can be obtained respectively from Eqs.(10.14) and (10.15) by substituting for $\rho^{(n-k)}(t)$, $k=0,1,2,\ldots$ their steady-state values. Following the above procedure and using the quantum regression theorem, it is possible to write down general expressions for multitime correlation functions. For instance for the four-time correlation function of the dipole moment operator we have

$$\langle p_\nu(t)p_\mu(t+\tau)p_\mu(t+\tau)p_\nu(t)\rangle = \mathrm{Tr}\left\{d^\mu d^\mu\, S(t+\tau,t).\, d^\nu\, \rho(t) d^\nu\right\}\ , \tag{10.16}$$

where $S(t+\tau,t)$ is given by Eq.(10.3) or Eqs.(10.4)-(10.5). Correlation functions such as in (10.16) are important in the study of the intensity-intensity correlations[23] in the light scattered by an atomic system. For many applications, the two-time correlation functions to second order in the external fields are important. Using (2.4) in (10.4), we can write down an explicit expression for the Laplace transform of the second-order correlation function $\hat{f}^{(2)}_{\mu\nu}(z,t)$ as follows:

$$\hat{f}^{(2)}_{\mu\nu}(z,t) = \sum_{ijk\ell} d^\mu_{ij} d^\nu_{k\ell} \left\{ i\delta_{jk}(iz-\Lambda_{ji})^{-1}\, \rho^{(2)}_{\ell i}(t) \right.$$

$$\left. + \frac{1}{2\pi} \sum_\alpha \int_{-\infty}^{\infty} d\omega_1\, e^{-i\omega_1 t}\, E_\alpha(\omega_1)\, A_{ijk\ell}(z,\, t,\, \omega_1) \right.$$

$$+ \frac{1}{2}\left(\frac{1}{2\pi}\right)^2 \sum_{\alpha\beta}^{-} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 e^{-i(\omega_1+\omega_2)t} E_\alpha(\omega_1)E_\beta(\omega_2)$$

$$\times B_{ijk\ell}(z, t, \omega_1, \omega_2)\Big\} , \qquad (10.17)$$

where $A_{ijk\ell}$ and $B_{ijk\ell}$ stand for

$$A_{ijk\ell}(z,t,\omega_1) = i(iz-\Lambda_{ji})^{-1}\Big[\sum_n^{-} d^{\alpha}_{ni}\delta_{kj}\rho^{(1)}_{\ell n}(t)(iz-\omega_1-\Lambda_{kn})^{-1}$$

$$- d^{\alpha}_{jk}\rho^{(1)}_{\ell i}(t)(iz-\omega_1-\Lambda_{ki})^{-1} + d^{\alpha}_{ji}\rho^{(1)}_{\ell k}(t)\left[C_{ki}(iz-\omega_1)-C_{kj}(iz-\omega_1)\right]\Big] \qquad (10.18)$$

and

$$B_{ijk\ell}(z,t,\omega_1,\omega_2) = i(iz-\Lambda_{ji})^{-1}(iz-\omega_1-\omega_2-\Lambda_{k\ell})^{-1}\rho^{(0)}_{\ell\ell}$$

$$\times\Big[\sum_n^{-}\left(d^{\alpha}_{jn}d^{\beta}_{nk}\delta_{\ell i}(iz-\omega_1-\Lambda_{ni})^{-1} + d^{\alpha}_{ni}d^{\beta}_{\ell n}\delta_{jk}(iz-\omega_1-\Lambda_{kn})^{-1}\right)$$

$$-\left(d^{\alpha}_{\ell i}d^{\beta}_{jk}(iz-\omega_1-\Lambda_{j\ell})^{-1} + d^{\alpha}_{jk}d^{\beta}_{\ell i}(iz-\omega_1-\Lambda_{ki})^{-1}\right)$$

$$+ d^{\alpha}_{ji}d^{\beta}_{\ell k}\left[C_{\ell j}(iz-\omega_1)-C_{\ell i}(iz-\omega_1)- C_{kj}(iz-\omega_1+ C_{ki}(iz-\omega_1)\right)$$

$$+ (\alpha, \omega_1) \leftrightarrow (\beta, \omega_2)\Big] \qquad (10.19)$$

Note that the C terms in (10.18) and (10.19) are as defined in Eq. (2.36) and they correspond to the extra contributions coming from

the inelastic collisions and spontaneous emission. A similar expression can be written down for $\hat{g}^{(2)}_{\mu\nu}$ [Eq.(10.15)]. We have

$$\hat{g}^{(2)}_{\mu\nu}(z,t) = \sum_{ijk\ell}^{-} d^{\mu}_{ij} d^{\nu}_{k\ell} \Big\{ i\delta_{\ell i}(iz-\Lambda_{ji})^{-1} \rho^{(2)}_{jk}(t)$$

$$+ \frac{1}{2\pi} \sum_{\alpha}^{-} \int_{-\infty} d\omega_1 \, e^{-i\omega_1 t} E_{\alpha}(\omega_1) A'_{ijk\ell}(z, t, \omega_1)$$

$$+ \frac{1}{2} \left(\frac{1}{2\pi}\right)^2 \sum_{\alpha\beta}^{-} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 e^{-i(\omega_1+\omega_2)t} E_{\alpha}(\omega_1) E_{\beta}(\omega_2) \cdot$$

$$\times B'_{ijk\ell}(z, t, \omega_1, \omega_2) \Big\} , \qquad (10.20)$$

where

$$A'_{ijk\ell}(z,t,\omega_1) = i(iz-\Lambda_{ji})^{-1} \Big[d^{\alpha}_{\ell i} \rho^{(1)}_{jk}(t)(iz-\omega_1-\Lambda_{j\ell})^{-1}$$

$$- \sum_{n}^{-} d^{\alpha}_{jn} \delta_{\ell i} \rho^{(1)}_{nk}(t)(iz-\omega_1-\Lambda_{ni})^{-1}$$

$$+ d^{\alpha}_{ji} \rho^{(1)}_{\ell k}(t) \left[C_{\ell j}(iz-\omega_1) - C_{\ell i}(iz-\omega_1)\right] \Big] , \qquad (10.21)$$

and $B'_{ijk\ell}$ is as given by (10.19) but with $\rho^{(o)}_{\ell\ell}$ interchanged by $\rho^{(o)}_{kk}$. In the radiative relaxation case, our result (10.17)-(10.19)when inverted reduces to the expression derived by Agarwal[80] in the context of the anomalous coherence functions of a system driven by a weak coherent field. One can obtain the steady-

state correlation functions $\hat{f}^{(2)}_{\mu\nu}(z) \equiv \underset{t\to\infty}{Lt}\, \hat{f}^{(2)}_{\mu\nu}(z,t)$ and $\hat{g}^{(2)}_{\mu\nu}(z) \equiv \underset{t\to\infty}{Lt}\, \hat{g}^{(2)}_{\mu\nu}(z,t)$ respectively from Eqs.(10.17) and (10.20) by replacing $\rho^{(2)}_{ij}(t)$, $\rho^{(1)}_{ij}$ etc., by their steady-state values. The expressions (10.17) and (10.20) are quite useful in computing the various two-time correlation functions that are important in describing the spectral properties of the light scattered by a multilevel system. For example, the fluorescence spectrum $S(\omega)$ is given by the relation

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{-i\omega\tau} \langle p^-(\tau)\, p^+(o) \rangle \quad , \tag{10.22}$$

where the p^+ and p^- are defined by

$$p^+ = \sum_{ij}^{-} d_{ij} |i\rangle\langle j| \quad , \quad E_i < E_j \quad ,$$

$$p^- = \sum_{ij}^{-} d_{ij} |i\rangle\langle j| \quad , \quad E_i > E_j \quad . \tag{10.23}$$

Since it is generally true that $\langle p^-(\tau)p^+(o)\rangle = \langle p^-(-\tau)p^+(o)\rangle^*$, one can express $S(\omega)$ in terms of the Laplace transform of $\langle p^-(\tau)p^+(o)\rangle$ as[21]

$$S(\omega) = 2\mathrm{Re}\, \hat{f}_{-+}(i\omega) \quad . \tag{10.24}$$

The spectral properties of the scattered light are also determined in terms of the Fourier transform of the anomalous correlator[83] $\langle p^+(\tau)p^+(o)\rangle$, which we define as

$$S_a(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \langle p^+(\tau)p^+(o)\rangle \quad . \tag{10.25}$$

As has been shown by Kazantsev et al,[83] the anomalous correlator $\langle E^+(\tau)E^+(o)\rangle$ is actually determined by the dipole correlation function $\langle p^+(|\tau|)p^+(o)\rangle$, and hence one can express $S_a(\omega)$ in terms of the Laplace transform of $\langle p^+(\tau)p^+(o)\rangle$ as

$$S_a(\omega) = \hat{f}_{++}(i\omega) + \hat{f}_{++}(-i\omega) \quad . \tag{10.26}$$

Thus in the case when the exciting field is weak, one can compute the quantities $S(\omega)$ and $S_a(\omega)$ for a multilevel system using the expressions (10.17)-(10.19). By looking at the structure of the expressions (10.17)-(10.19) it is possible to make a few general remarks about the spectral functions $S(\omega)$ and $S_a(\omega)$. Note that in Eq.(10.18), the contribution from the zero eigenvalue of the population relaxation matrix R to the C terms does not cancel. This can be understood by noting that in general, the contribution from the zero eigenvalue to $B_{|J}(\omega)$ is equal to $\rho^{(o)}_{JJ}/\omega$, where $\rho^{(o)}_{JJ}$ is the thermal equilibrium population of the level $|J\rangle$. Thus the zero eigenvalue contribution in the expression (10.18) determines the elastic or the coherent contribution to the spectral functions $S(\omega)$ and $S_a(\omega)$. The remaining terms in the expressions (10.17)-(10.19) determine the inelastic or the incoherent components in $S(\omega)$ and $S_a(\omega)$. The correlation functions $\langle p^-(\tau)p^+(o)\rangle$ and $\langle p^+(\tau)p^+(o)\rangle$ are also important for the determination of the quantum mechanical properties of the fields generated in a multilevel system. The quantum theory of nonlinear mixing[84]

requires not only the classical quantities which are determined in terms of the nonlinear susceptibilities, but also certain purely quantum mechanical quantities which are related to the anticommutators of correlations functions such as $\langle[p^-(\tau),p^+(o)]\rangle$ and $\langle[p^+(\tau),p^+(o)]\rangle$. In the next section we specialize our general result (10.17)- (10.19) to the case of a two-level system and discuss the effect of collisions on the normal and anomalous correlation functions and on the spectral functions $S(\omega)$ and $S_a(\omega)$.

III. EFFECT OF COLLISIONS ON THE CORRELATION FUNCTIONS OF A TWO-LEVEL SYSTEM

Consider a two-level system [see Fig.(1)] to be interacting with a weak exciting field $\vec{E}$, where $\vec{E}$ is given by

$$\vec{E}(t) = \hat{e}(e_\ell e^{-i\omega_\ell t} + c.c.) \quad . \tag{10.27}$$

We assume that the collision-induced transitions from the ground state $|2\rangle$ to the excited state $|1\rangle$ can be neglected and hence we put $\gamma_{12}=0$. The correlation function that determines the fluorescence spectrum of a two-level atom is $\langle p^-(\tau)p^+(o)\rangle$ where $p^-=\vec{d}_{12}.\hat{e}|1\rangle\langle 2|$ and $p^+=\vec{d}_{21}.\hat{e}|2\rangle\langle 1|$. The Laplace transform of $\langle p^-(\tau)p^+(o)\rangle$ to second order in the exciting field can be computed from Eqs.(10.17)-(10.10), and is given by

$$\hat{f}^{(2)}_{-+}(z) = \frac{|g_\ell|^2 |d_{12}|^2}{\Delta^2+\Gamma_{12}^2} \left[\frac{1}{z+i\omega_\ell} + \frac{2\Gamma_{12}^{ph}/\gamma_{21}}{z-i\omega_{12}+\Gamma_{12}} \right] ,$$

$$g_\ell = \left(\vec{d}_{12} \hat{e} \right) e_\ell , \quad \Delta = \omega_\ell - \omega_{12} , \quad \Gamma_{12} = \frac{1}{2}\gamma_{21} + \Gamma_{12}^{ph} \qquad (10.28)$$

Here Γ_{12}^{ph} is the rate of phase-changing collisions. The expression in (10.28) can be easily inverted to yield the correlation function

$$\langle p^-(\tau)p^+(o)\rangle^{(2)} = \frac{|g_\ell|^2 |d_{12}|^2}{\Delta^2+\Gamma_{12}^2} e^{i\omega_\ell \tau} \left[1 + \frac{2\Gamma_{12}^{ph}}{\gamma_{21}} e^{-(i\Delta+\Gamma_{12})\tau} \right] ,$$

$$\tau > 0 \qquad (10.29)$$

The expression for $\langle p^-(\tau)p^+(o)\rangle^{(2)}$ for $\tau<0$ can be obtained from Eq.(10.29) by noting that $\langle p^-(-\tau)p^+(o)\rangle = \langle p^-(\tau)p^+(o)\rangle^*$. As has been shown by Reynaud et al,[79] the quantity $|\langle p^-(\tau)p^+(o)\rangle|^2$ is important for studying the correlation properties of photons emitted in the same direction from a system that is excited by two counter-propagating pumps. In particular such a quantity shows the bunching of the photons, i.e., $|\langle p^-(\tau)p^+(o)\rangle|^2$ is maximum for $\tau=0$. Thus the expression in (10.29) enables us to study the effect of phase-changing collisions on the bunching behavior of photons emitted by a two-level atom. The fluorescence spectrum $S(\omega)$ follows from Eqs.(10.28) and (10.24) and is given by

$$S(\omega) = \frac{|g_\ell|^2 |d_{12}|^2}{\Delta^2+\Gamma_{12}^2} \left\{ \delta(\omega-\omega_\ell) + \frac{(2\Gamma_{12}^{ph}/\pi\gamma_{21})\Gamma_{12}}{(\omega-\omega_{12})^2+\Gamma_{12}^2} \right\} . \qquad (10.30)$$

One can see from Eq.(10.30) that in the absence of phase-changing collisions ($\Gamma_{12}^{ph}=0$), the fluorescence spectrum consists of only the elastically scattered component at $\omega=\omega_\ell$ [proportional to $\delta(\omega-\omega_\ell)$]. However, the phase-changing collisions give rise to an additional (redistributed) component at $\omega=\omega_{12}$. Thus our result (10.30) explains the well-known phenomena of collisional redistribution of radiation.[25]

Next we discuss the effect of collisions on the anomalous correlator for the two-level atom. It follows from Eqs.(10.17)-(10.19) that the Laplace transform of the correlation function $\langle p^+(\tau)p^+(o)\rangle^{(2)}$ is given by

$$\hat{f}^{(2)}_{++}(z) = \frac{d_{21}^2 g_\ell^2 e^{-2i\omega_\ell t}}{\nu_-^2}\left[\frac{-1}{z+i\omega_\ell} + \frac{1}{z+i\omega_\ell+\nu_-}\right] ,$$

$$\nu_- = -i\Delta + \Gamma_{12} \qquad (10.31)$$

Hence the correlation function $\langle p^+(\tau)p^+(o)\rangle^{(2)}$ can be obtained by inverting the expression in (10.31) and is given by

$$\langle p^+(\tau)p^+(o)\rangle^{(2)} = \frac{d_{21}^2 g_\ell^2 e^{-2i\omega_\ell t - i\omega_\ell \tau}}{\nu_-^2}\left[-1 + e^{-\nu_-|\tau|}\right] . \qquad (10.32)$$

The quantity $|\langle p^+(\tau)p^+(o)\rangle|^2$ again is important in the study of the correlation properties of photons emitted in opposite directions.[79] Note that for $\tau=0$, the expression in (10.32) becomes zero. This shows the antibunching behavior of the emitted photons.

The spectral function $S_a(\omega)$ follows from (10.31) and (10.26) and is given by[83]

$$S_a(\omega) = \frac{d_{21}^2 g_\ell^2 e^{-2i\omega_\ell t}}{2\pi\nu_-^2}\left[-2\pi\delta(\omega-\omega_\ell) + \frac{1}{\nu_- + i(\omega-\omega_\ell)} + \frac{1}{\nu_- - i(\omega-\omega_\ell)}\right] \tag{10.33}$$

Note that unlike the fluorescence spectrum $S(\omega)$ which is real, the spectral function $S_a(\omega)$ in general is complex. Kazantsev et al[83] have argued that both the real as well as the imaginary parts of $S_a(\omega)$ are important for the determination of the spectral properties of the scattered light. It can be seen that $S_a(\omega)$ contains the inelastic components at $\omega-\omega_\ell = \pm\Delta$ even in the absence of collisions. Thus the quantity $S_a(\omega)$ contains more information about the spectral properties of scattered light than the fluorescence spectrum $S(\omega)$. To second order in the exciting field, the phase-changing collisions do not give rise to any new feature in $S_a(\omega)$. However to fourth order in the exciting field (second order in the intensity) the effect of phase-changing collisions is found to be drastic. Using the general result (10.14) and the relation (10.26) we have shown that to fourth order in the exciting field, $S_a(\omega)$ has the following structure:

$$S_a(\omega) = \frac{4|g_\ell|^2 d_{21}^2 g_\ell^2 e^{-2i\omega_\ell t}}{2\pi\nu_-^2|\nu_-|^2}\left\{2\pi\delta(\Omega)\left(1+\frac{2\Gamma_{12}^{ph}}{\gamma_{21}}\right)\right.$$

$$\left. - \left(1+\frac{2\Gamma_{12}^{ph}}{\gamma_{21}}\right)\left(\frac{1}{\nu_- + i\Omega} - \frac{\nu_-/2}{(\nu_- + i\Omega)^2}\right) + \frac{1}{(\gamma_{21}+i\Omega)(\nu_- + i\Omega)}\right.$$

$$\times \quad \left\{ \frac{1}{\nu_+ + i\Omega} - \frac{1}{\nu_- + i\Omega} \right\} + \text{terms with } \Omega \leftrightarrow -\Omega \Big\} \ ,$$

$$\Omega = \omega - \omega_\ell \ , \ \nu_\pm = \pm i\Delta + \Gamma_{12} \ . \qquad (10.34)$$

Thus we can see from the expression in (10.34) that to fourth order in the exciting field, the phase-changing collisions enhance the usual terms by a factor $(1 + 2\Gamma_{12}^{ph}/\gamma_{21})$.

IV. TWO-TIME CORRELATION FUNCTIONS IN PRESENCE OF STRONG FIELDS

The dynamics of a quantum mechanical system interacting with a reservior and with a strong field and a weak field is described by the equation [as in Eq.(7.1)]

$$\frac{\partial \rho}{\partial t} = -i[H_o + V(t) + F(t), \rho] + L_R \rho \ , \qquad (10.35)$$

which on making the canonical transformations with U(t) and S [as in Eqs.(7.2)-(7.6)] and on making the dressed-atom approximation becomes

$$\frac{\partial \tilde{\rho}}{\partial t} = -i [\beta, \tilde{\rho}] - i[\tilde{F}(t), \tilde{\rho}] + L_D \tilde{\rho} \ , \qquad (10.36)$$

where

$$\beta = S^{-1} \tilde{h} S \ , \ \tilde{F}(t) = U^{-1}(t) S^{-1} F(t) S U,$$

$$\tilde{h} = U^{-1}(t) [H_o + V(t)] U(t) + i \left(\frac{\partial U^{-1}}{\partial t} \right) U \qquad (10.37)$$

Here $L_D\overset{*}{\rho}$ contains the intensity-dependent relaxation parameters and is given by [Eq.(7.8)], i.e.,

$$(L_D\overset{*}{\rho})_{ij} = -q_{ij}\overset{*}{\rho}_{ij}(1-\delta_{ij}) + \delta_{ij}\sum_k (p_{ik}\overset{*}{\rho}_{kk} - p_{ki}\overset{*}{\rho}_{ii}) \qquad (10.38)$$

To zeroeth order in the weak field and to all orders in the dressing field it follows from (10.36) that

$$\overset{*}{\rho}^{(o)}(t+\tau) = e^{L_o\tau}\overset{*}{\rho}^{(o)}(t) \quad , \quad \tau > 0 \quad , \qquad (10.39)$$

where we have defined

$$L_o \equiv -i[\beta, \ ] + L_D \quad . \qquad (10.40)$$

Hence the expectation value of the physical observable A at time $t+\tau$ is given by

$$\langle A(t+\tau)\rangle^{(o)} = Tr\left\{ A\rho^{(o)}(t+\tau) \right\} \quad ,$$

$$= Tr\left\{ \overset{*}{A}(t+\tau)\overset{*}{\rho}^{(o)}(t+\tau) \right\}$$

$$\overset{*}{A}(t+\tau) = S^{-1}U^{-1}(t+\tau)AU(t+\tau)S \quad . \qquad (10.41)$$

On using (10.39), the equation (10.41) becomes

$$\langle A(t+\tau)\rangle^{(o)} = Tr\left\{ \overset{*}{A}(t+\tau)\, e^{L_o\tau}\overset{*}{\rho}^{(o)}(t) \right\} \quad ,$$

$$\overset{*}{B}(t) = S^{-1}U^{-1}(t)BU(t)S \quad . \qquad (10.42)$$

Similarly one can write down an expression for $\langle B(t)A(t+\tau)\rangle^{(o)}$ and this is given by

$$\langle B(t)A(t+\tau)\rangle^{(o)} = Tr\left\{ \overset{\approx}{A}(t+\tau)\, e^{L_o\tau}\, \overset{\approx}{\rho}^{(o)}(t)\overset{\approx}{B}(t) \right\} . \qquad (10.43)$$

Following the procedure as above one can write down similar expressions for the correlation functions when $\tau < 0$. Thus we have

$$\langle A(t+\tau)B(t)\rangle^{(o)} = Tr\left\{ \overset{\approx}{B}(t)\, e^{-L_o\tau}\, \overset{\approx}{\rho}^{(o)}(t+\tau)\overset{\approx}{A}(t+\tau) \right\} ,$$

$$\langle B(t)A(t+\tau)\rangle^{(o)} = Tr\left\{ \overset{\approx}{B}(t)\, e^{-L_o\tau}\, \overset{\approx}{A}^{(o)}(t+\tau)\overset{\approx}{\rho}(t+\tau) \right\} ,$$

$$\tau < 0 \qquad (10.44)$$

Thus by using the expressions (10.42)-(10.44) one can compute the various two-time correlation functions of a system that is excited by an intense field. For the case of a two-level system interacting with a strong field ω_ℓ, the correlation function $\langle p^-(\tau)p^+(o)\rangle$ will be given by (10.42) with $A \to p^- = \vec{d}_{12}.\hat{e}|1\rangle\langle 2|$ and $B \to p^+ = \vec{d}_{21}.\hat{e}|2\rangle\langle 1|$, where $\hat{e}$ is the polarization vector of the strong field. Using the expressions for the various parameters in the dressed-atom picture for the case of two-level atom which we have already derived in Chapter VII, we have shown that

$$\langle p^-(\tau)p^+(o)\rangle = |\, d_{12}\,|^2\, e^{i\omega_\ell\tau}\left\{ \sin^2\theta\cos^2\theta\left[\left(\overset{\approx}{\rho}^{(o)}_{11} - \overset{\approx}{\rho}^{(o)}_{22} \right)^2 \right.\right.$$

$$+ \; 4\rho_{11}^{*(o)}\rho_{22}^{*(o)} \, e^{-\tilde{\gamma}_1\tau} + \cos^4\theta \, \rho_{11}^{*(o)} \, e^{-i\tilde{\Lambda}_{21}\tau}$$

$$+ \sin^4\theta \, \rho_{22}^{*(o)} \, e^{-i\tilde{\Lambda}_{12}\tau} \Big\} \quad ,$$

$$\tilde{\gamma}_1 = p_{12} + p_{21} \quad , \; \tilde{\Lambda}_{12} = \Omega_R - iq_{12}, \; \tilde{\Lambda}_{21} = -\Omega_R - iq_{12} \qquad (10.45)$$

The fluorescence spectrum of the two-level atom which is given by the Fourier transform of the expreesion in (10.45) is then given by

$$S(\omega) = |d_{12}|^2 \Big\{ \sin^2\theta \cos^2\theta \Big(\rho_{11}^{*(o)} - \rho_{22}^{*(o)} \Big)^2 \delta(\Omega)$$

$$+ \frac{4\rho_{11}^{(o)}\rho_{22}^{*(o)}(\tilde{\gamma}_1/\pi)}{(\Omega^2+\tilde{\gamma}_1^2)} + \frac{\cos^4\theta \, \rho_{11}^{*(o)}(q_{12}/\pi)}{(\Omega - \Omega_R)^2 + q_{12}^2} + \frac{\sin^4\theta \, \rho_{22}^{*(o)}(q_{12}/\pi)}{(\Omega + \Omega_R)^2 + q_{12}^2} \Big\},$$

$$\Omega = \omega - \omega_\ell \quad . \qquad (10.46)$$

In the case when the exciting field is at resonance with the optical transition ($\Delta=0$), $S(\omega)$ réduces to

$$S(\omega) = \frac{|d_{12}|^2}{4} \Bigg[\frac{1/\pi T_2}{(\Omega^2 + 1/T_2^2)} + \frac{1}{2} \Bigg[\frac{\frac{1}{2\pi}(\frac{1}{T_1} + \frac{1}{T_2})}{(\Omega-2G)^2 + \frac{1}{4}(\frac{1}{T_1} + \frac{1}{T_2})^2}$$

$$+ \frac{\frac{1}{2\pi}(\frac{1}{T_1} + \frac{1}{T_2})}{(\Omega+2G)^2 + \frac{1}{4}(\frac{1}{T_1} + \frac{1}{T_2})^2} \Bigg) \Bigg] \quad ,$$

$$T_1^{-1} = \gamma_{12}+\gamma_{12} \ , \quad T_2^{-1} = \frac{1}{2}\left(\gamma_{12}+ \gamma_{21} \right) + \Gamma_{12}^{ph} \ , \qquad (10.47)$$

where T_1 and T_2 are respectively the longitudinal and transverse relaxation times of a two-level atom. Thus the expression (10.47) explains the well-known triplet structure in the resonance fluorescence spectrum of a two-level atom.[21] The expression (10.47) clearly shows that in presence of collisions, the central component at $\Omega=0$ has a width T_2^{-1} while the Rabi side bands at $\Omega=\pm 2G$ have a width equal to $\frac{1}{2}(\frac{1}{T_1} + \frac{1}{T_2})$. Similarly, one can obtain the anomalous correlation function $\langle p^+(\tau)p^+(o)\rangle$ from (10.43) and this is given by

$$\langle p^+(\tau)p^+(o)\rangle = d_{21}^2 e^{-2i\omega_\ell t - i\omega_\ell \tau - 2i\phi} \sin^2\theta\cos^2\theta$$

$$\times \left[\left(\rho_{11}^{*(o)} - \rho_{22}^{*(o)} \right)^2 + 4\, \rho_{11}^{*(o)} \rho_{22}^{*(o)}\, e^{-\tilde{\gamma}_1|\tau|} \right.$$

$$\left. - \left(\rho_{11}^{*(o)} e^{-i\tilde{\Lambda}_{21}|\tau|} + \rho_{22}^{*(o)} e^{-i\tilde{\Lambda}_{12}|\tau|} \right) \right] \ . \qquad (10.48)$$

Note that the expression in (10.48) becomes zero for $\tau=0$ which shows the antibunching behavior of the sca ttered photons. The spectral function $S_a(\omega)$, which is given by the Fourier transform of the expression in (10.45) has the structure

$$S_a(\omega) = d_{21}^2\, e^{-2i\omega_\ell t - 2i\phi} \sin^2\theta\cos^2\theta \left[(\rho_{11}^{*} - \rho_{22}^{*(o)})^2 \delta(\Omega) \right.$$

$$+ \frac{4\rho_{11}^{s(o)}\rho_{22}^{s(o)}(\tilde{\gamma}_1/\pi)}{\Omega^2 + \tilde{\gamma}_1^2} - \frac{1}{2}\left[\frac{q_{12}/\pi}{(\Omega-\omega_R)^2 + q_{12}^2} + \frac{q_{12}/\pi}{(\Omega-\omega_R)^2 + q_{12}^2}\right]$$

$$- \frac{1}{2\pi}(\rho_{11}^{s(o)} - \rho_{22}^{s(o)})\left[\frac{\Omega+\Omega_R}{(\Omega+\Omega_R)^2+q_{12}^2} - \frac{\Omega-\Omega_R}{(\Omega-\Omega_R)^2+q_{12}^2}\right]\Bigg] ,$$

$$\Omega = \omega - \omega_\ell \quad . \tag{10.49}$$

In the case when the exciting field is resonant with the atomic transition, i.e., $\Delta=0$, Eq.(10.49) reduces to

$$S_a(\omega) = \frac{d_{21}^2 e^{-2i\omega_\ell t - 2i\phi}}{4}\left[\frac{1/\pi T_2}{(\Omega^2 + 1/T_2^2)} - \frac{1}{2}\left[\frac{\frac{1}{2\pi}(\frac{1}{T_1} + \frac{1}{T_2})}{(\Omega-2G)^2 + \frac{1}{4}(\frac{1}{T_1} + \frac{1}{T_2})^2}\right.\right.$$

$$\left.\left. + \frac{\frac{1}{2\pi}(\frac{1}{T_1} + \frac{1}{T_2})}{(\Omega+2G)^2 + \frac{1}{4}(\frac{1}{T_1} + \frac{1}{T_2})^2}\right]\right] . \tag{10.50}$$

Note that when $\Delta=0$, the imaginary part of the spectral function $S_a(\omega)$ vanishes under the dressed-atom approximation (i.e., in the strong-field limit) and only the real part survives. Note further that in this case $S_a(\omega)$ [Eq.(10.50)] has essentially the same structure as that of $S(\omega)$ in (10.47) except for a difference of sign in the second term.

Thus, in conclusion, we have developed a Liouville operator formulation of the two-time correlation functions of the dipole moment operator which are important for the description of the spectral and the quantum mecahanical properties of the generated fields. Explicit expressions for these correlation functions for a system undergoing phase-changing and inelastic collisions are obtained. Within the context of the two-level model, we have studied the effects of collisions on the fluorescence spectrum and the anomalous correlator, both under weak-field and strong-field conditions. To second order in the exciting field, our results explain the phenomena of the collisional redistribution of radiation. To fourth order in the exciting field, collisions lead to an enhancement of the coherent component in the Fourier transform of the anomalous correlator. In the case of strong excitation, our results explain the well-known triplet structure in the resonance fluorescence spectrum and the effects of collisions on this spectrum.

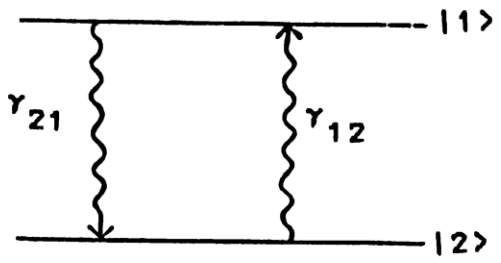


Fig.1. Energy diagram of a model two-level system. γ_{21} and γ_{12} are the relaxation rates from levels |1> to |2> and |2> to |1> respectively.

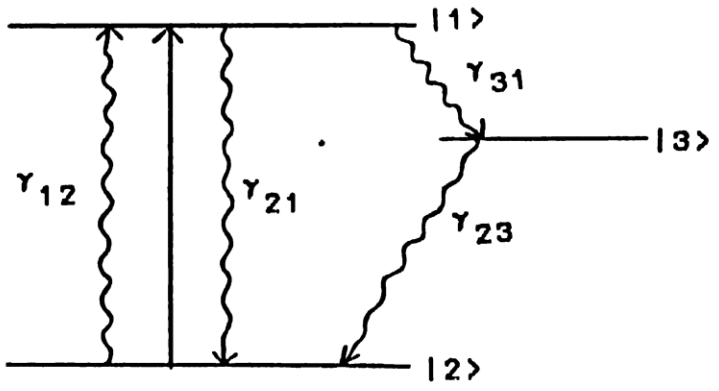


Fig.2. Energy diagram of the three-level model of ruby. The wavy arrows denote the relaxation-induced transitions. γ_{ij} denotes the relaxation rate from |j> to |i>. The straight arrow indicates the dipole transition.

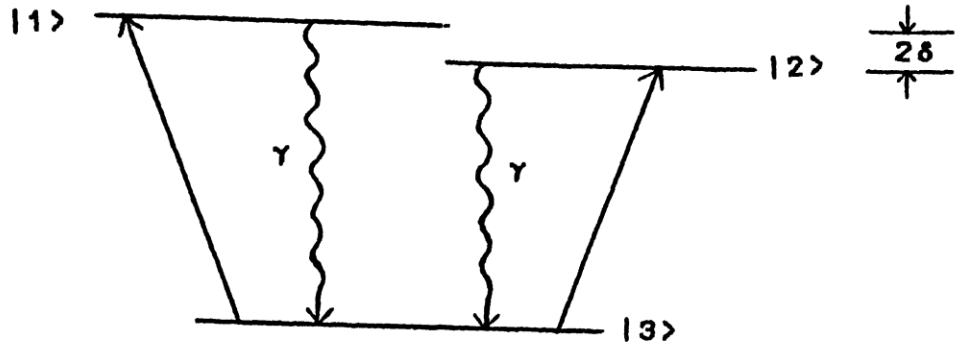


Fig.3. Energy diagram of V-type three-level system. γ is the decay rate of levels |1> and |2> to the ground level |3>.

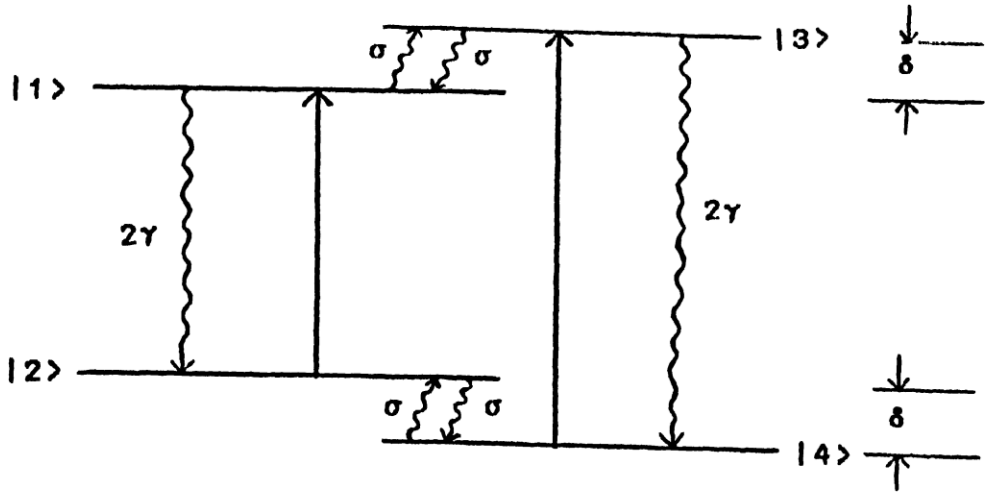


Fig.4. Energy diagram of the model four-level system with various relaxation rates. 2γ is the radiative relaxation rate of each transition and σ is the strength of collisional coupling between the two components.

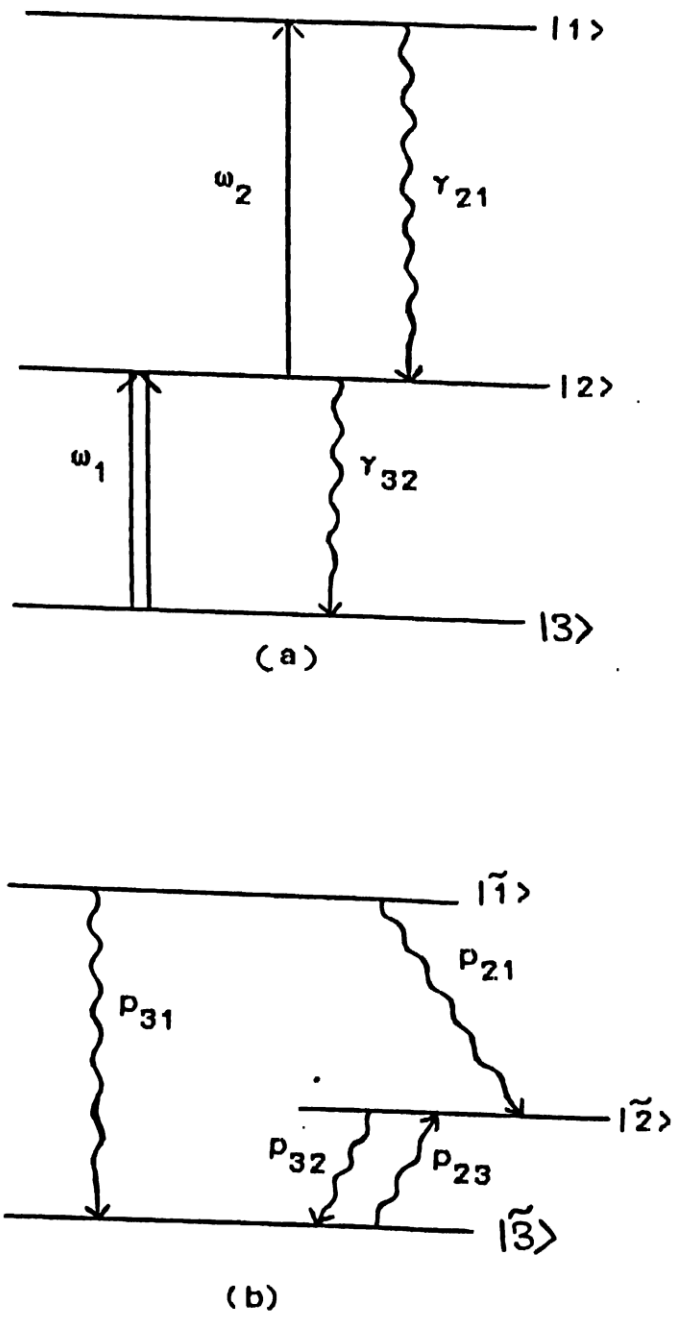


Fig.5. Schematic diagram of the model system in (a) the bare-atom picture and (b) the dressed-atom picture. In (a), $\gamma_{21}(\gamma_{32})$ is the radiative decay rate from $|1\rangle(|2\rangle)$ to $|2\rangle$ $(|3\rangle)$. In (b), the variouus p terms denote the field-dependent relaxation rates betweeen the dressed levels, as defined by Eq.(8.31).

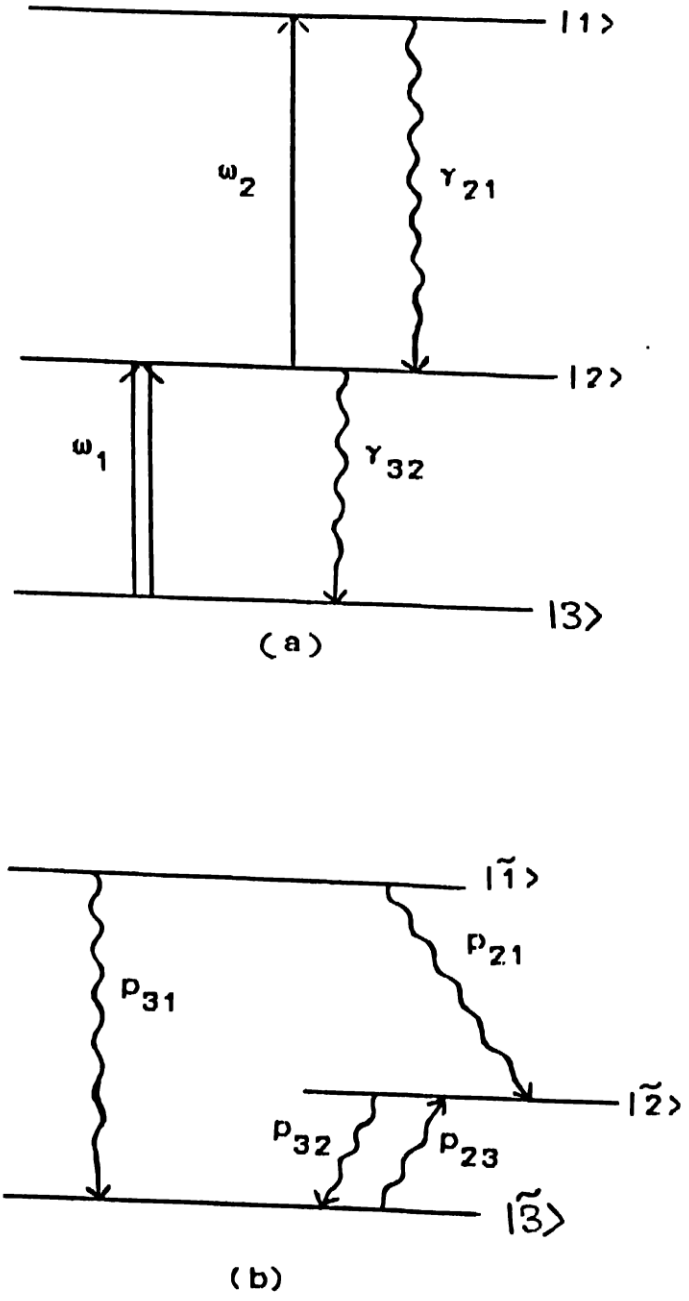


Fig.5. Schematic diagram of the model system in (a) the bare-atom picture and (b) the dressed-atom picture. In (a), $\gamma_{21}(\gamma_{32})$ is the radiative decay rate from $|1\rangle(|2\rangle)$ to $|2\rangle$ $(|3\rangle)$. In (b), the variouus p terms denote the field-dependent relaxation rates betweeen the dressed levels, as defined by Eq.(8.31).

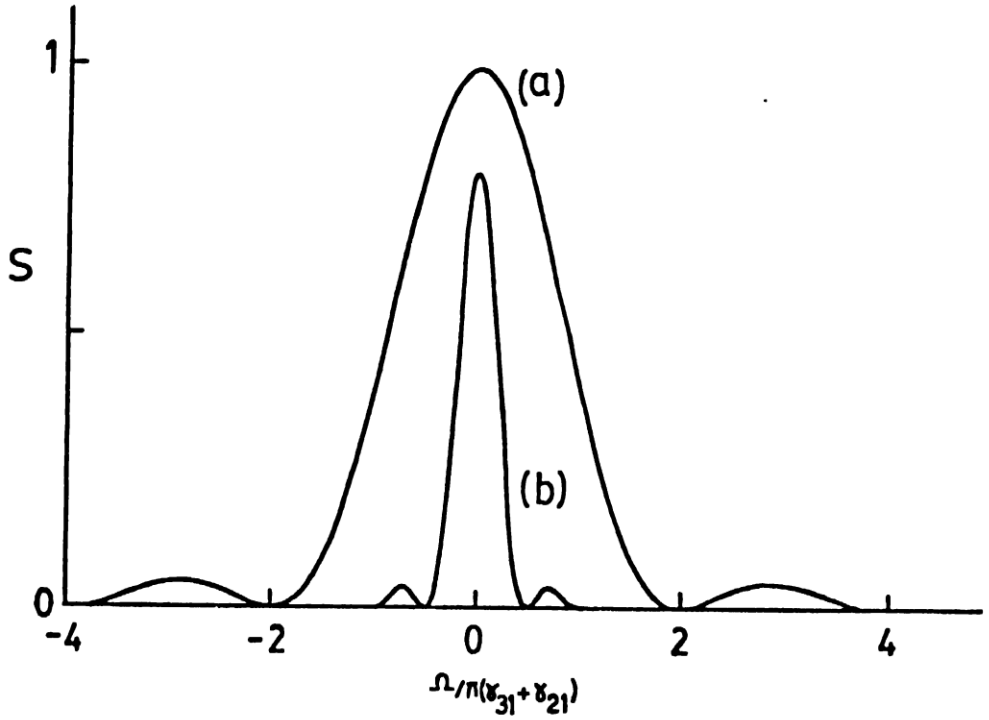


Fig.7. The transient FWM signal produced by Ruby. The parameters are $\gamma_{31}=2 \times 10^7$/sec, $\gamma_{21}=3 \times 10^5$/sec [Ref. 44], $\gamma_{23} = 10^3/3$/sec, $\Delta=1000(\gamma_{31} + \gamma_{21})$, $(\gamma_{31}+\gamma_{21})t$ = (a) 1.0, (b) 4.0. Both the curves are normalized to the peak height of curve (a).

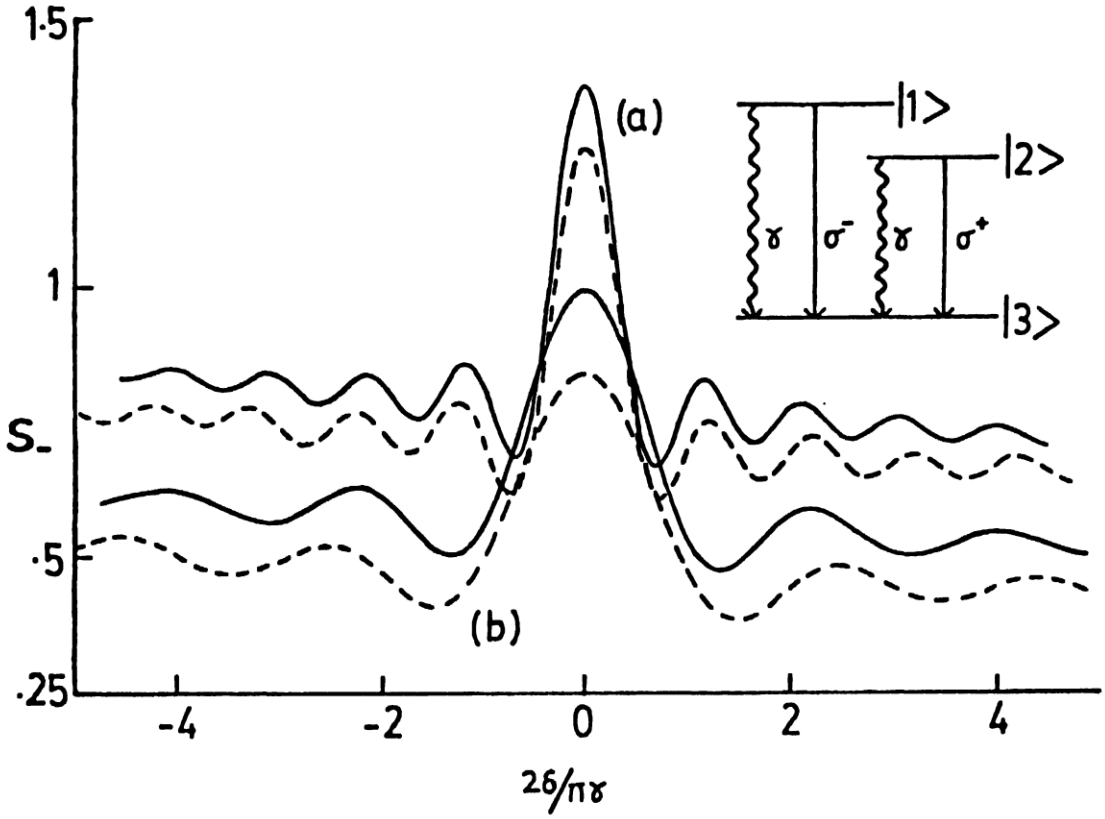


Fig.8. The transient Hanle resonance in FWM, produced by the transition J=0 to J=1 in phase conjugation geometry, as a function of the magnetic field for $\gamma t=0.05$ (a) and 0.1 (b). $\Delta=5000\gamma$. The solid (dashed) curves give the signal $S_-(\propto S_+)$ averaged (unaveraged) over the detector response time $\gamma t_d=0.01$. All curves are normalized to the peak height of solid curve (a). The scale on the x-axis is magnified by a factor 20.

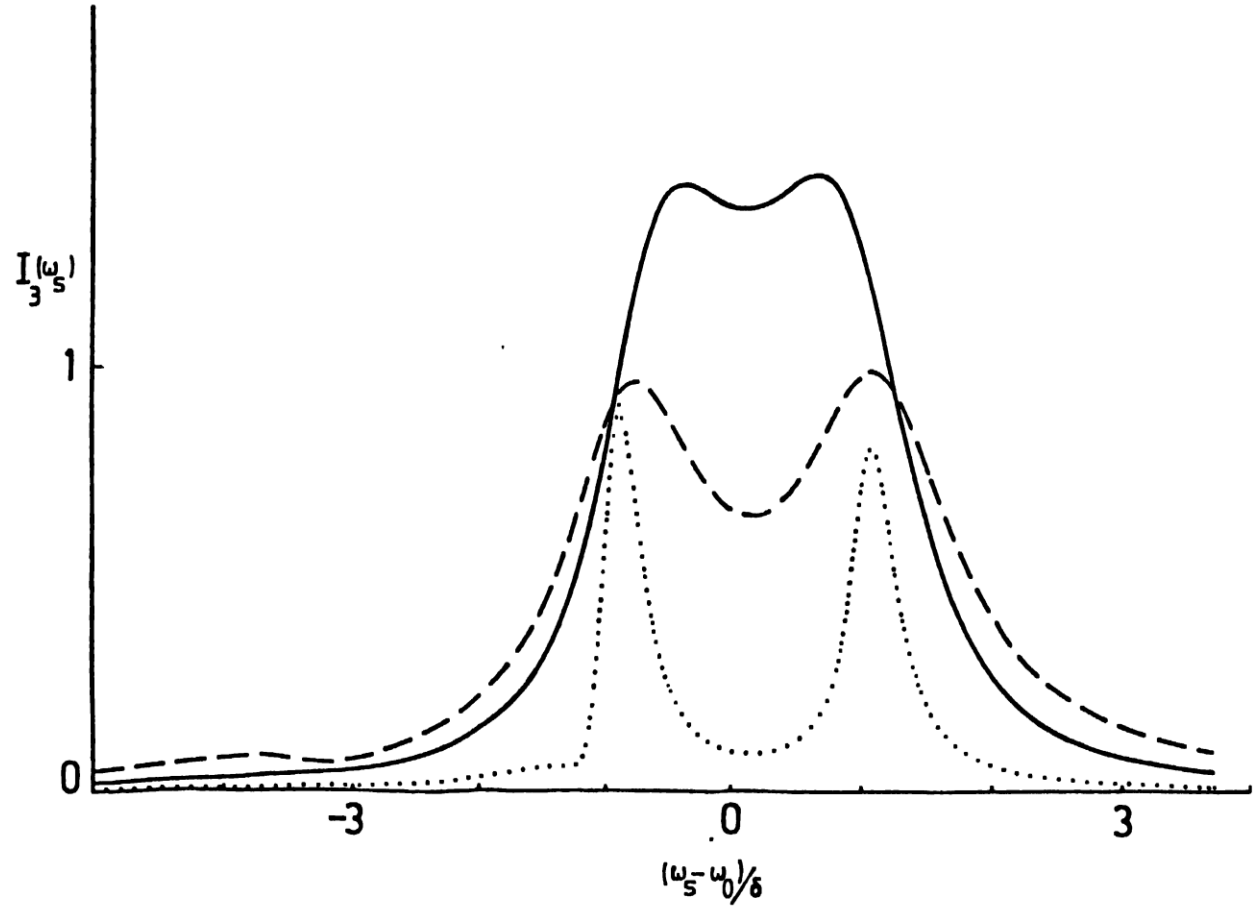


Fig.9. Saturated absorption spectrum $I_3(\omega_s)$ as a function $(\omega_s-\omega_o)/\delta$ for various parameters given by $\sigma/\delta=0.5$, $\sigma/\delta=0.25$, $\Delta_\ell=-7/2\delta$, $g/2\gamma=1.0$ ($g=de_\ell/\hbar$ is the pump strength). The solid (dashed) line corresponds to the spectrum with cross relaxation, $\xi=\sigma$ (without crossrelaxation, $\xi=0$); the dotted line denotes the case of no collisions ($\sigma=\xi=0$). The normalization in the last case is four times larger than what is shown in the figure.

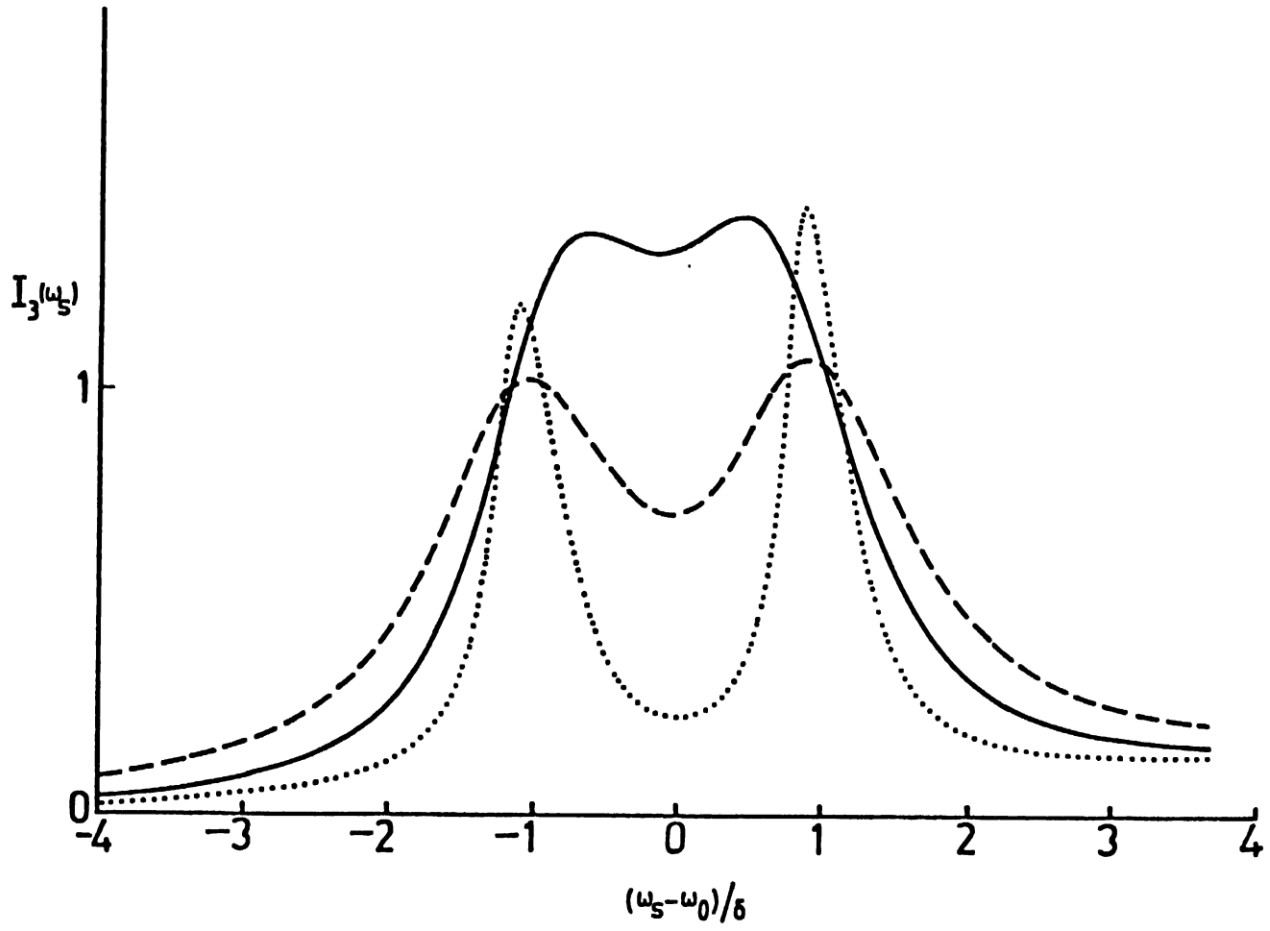


Fig.10. Same as Fig.9, except that now $\Delta_\ell=-\delta$ and $g/2\gamma=0.1$. The normalization in the case of no collisions ($\xi=\sigma=0$) is two times larger than what is shown in the figure.

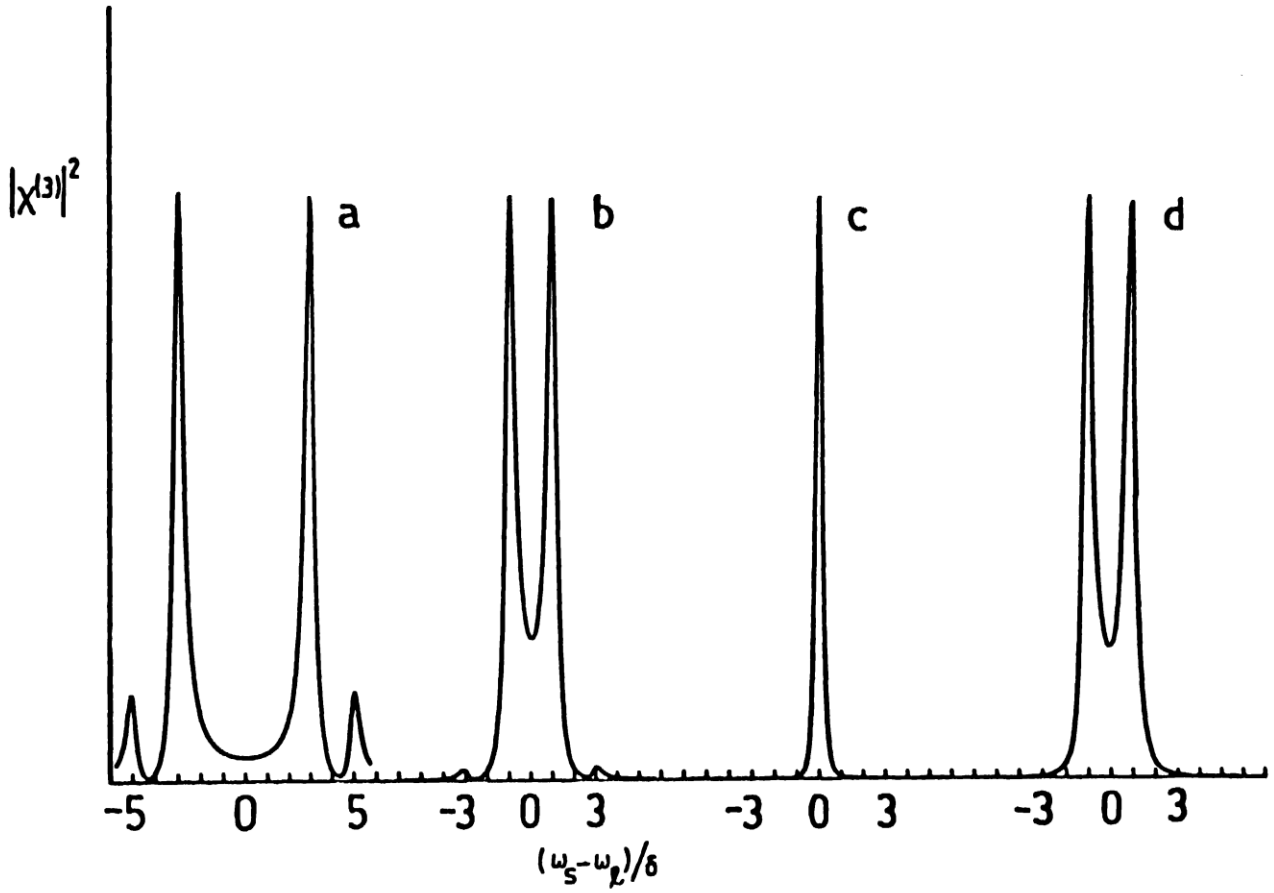


Fig.11. Four-wave mixing signal for the case of no collisions ($\sigma/\delta=\xi/\delta=0$) and $\gamma/\delta=0.25$ as a function of $(\omega_s-\omega_\ell)/\delta$. Different curves in this figure correspond to different values of pump detuning, Δ_ℓ = (a) -4δ, (b) -2δ, (c) $-\delta$, (d) 0.

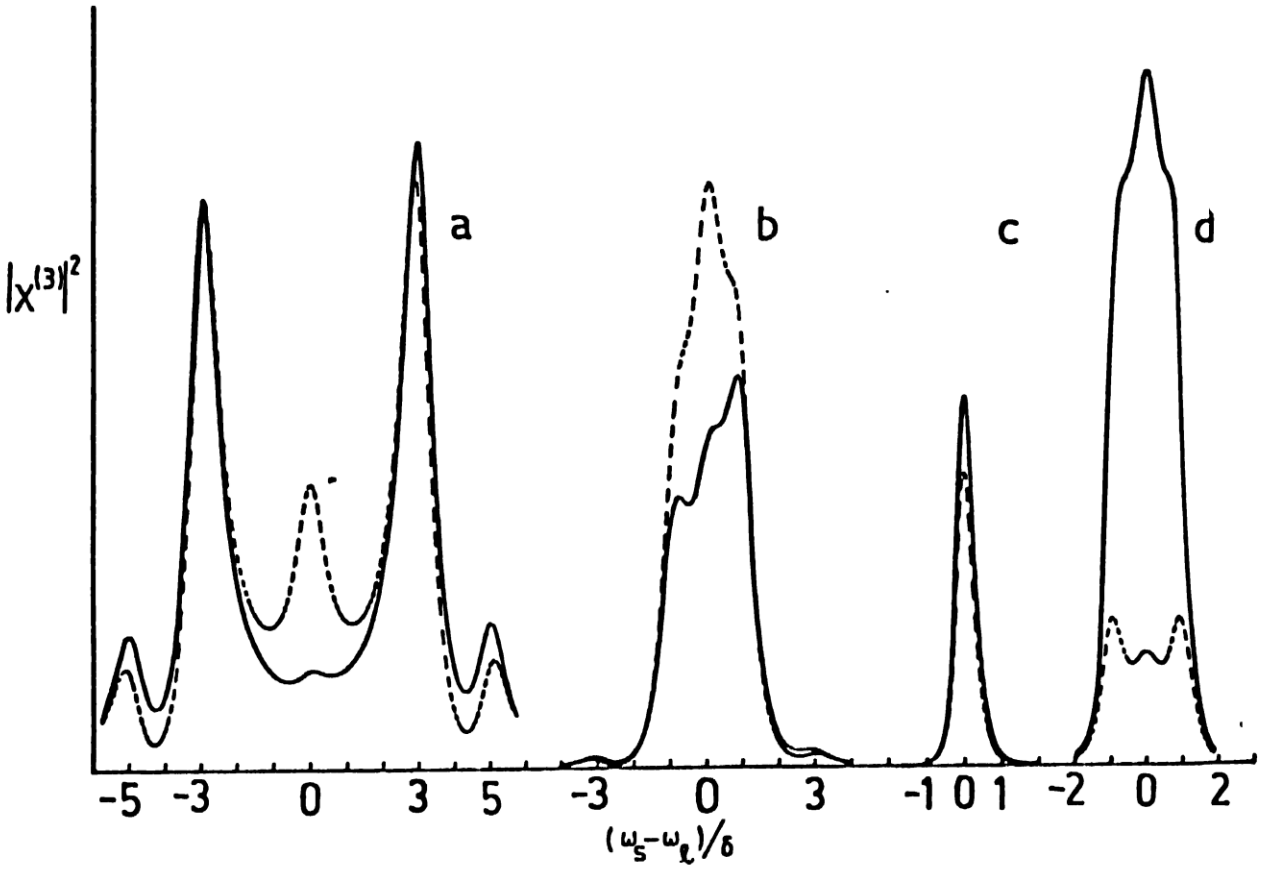


Fig.12. Effect of change in the rate of inelastic collisions on the four-wave mixing signal as a function of $(\omega_s-\omega_\ell)/\delta$. $\sigma/\delta=0.25$, $\gamma/\delta=0.25$. Solid (dashed) line corresponds to the case with cross-relaxation, $\xi=\sigma$ (without crossrelaxation, $\xi=0$). Different curves in this figure correspond to different values of pump detuning, Δ_ℓ=(a) -4δ, (b) -2δ, (c) $-\delta$, (d) 0. The normalization for curves (c) and (d) is, respectively, two and four times larger than what is shown in the figure.

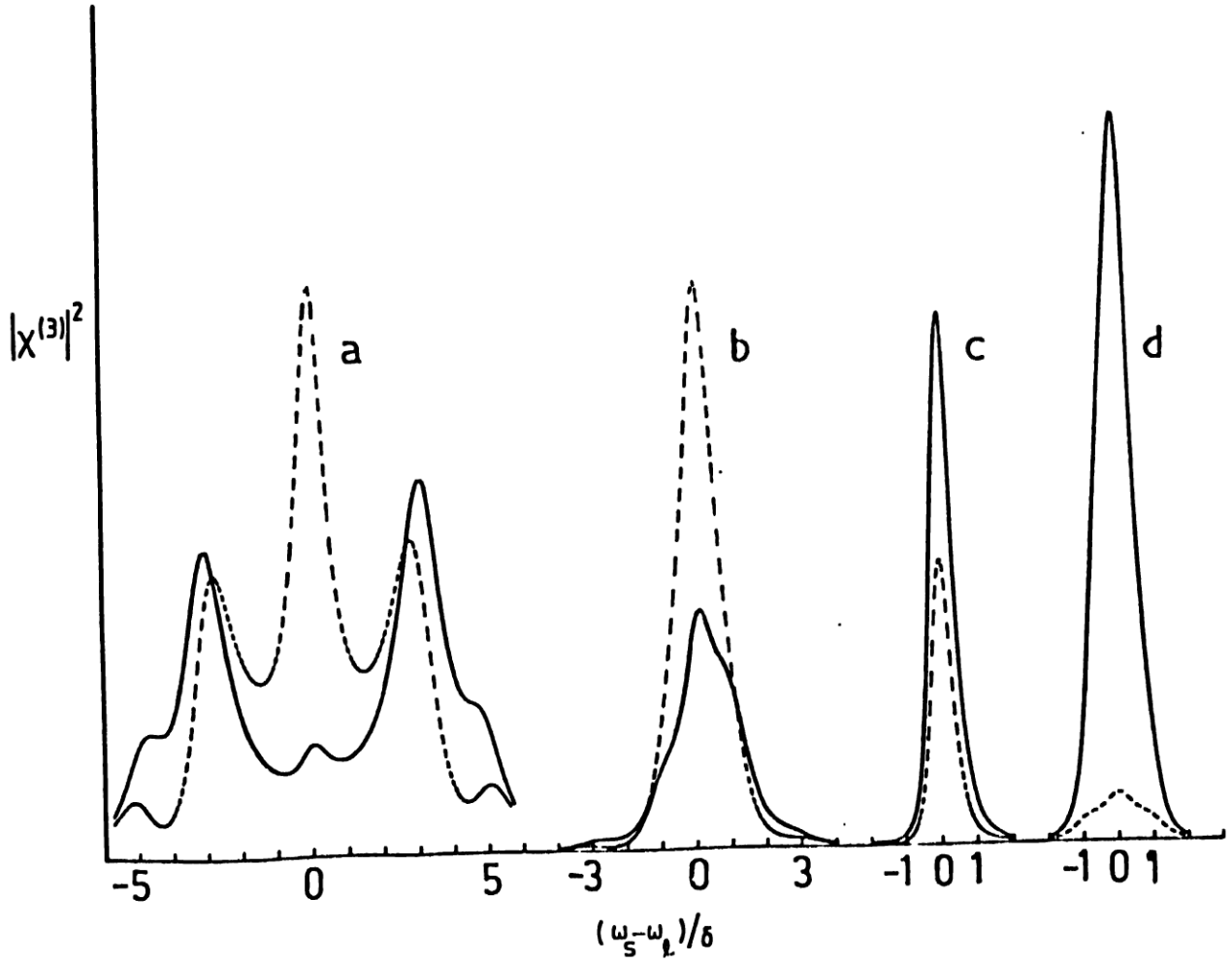


Fig.13. Same as in Fig.12 but for increased value of the rate of collisions $\sigma/\delta=0.5$. The normalization for curves (c) and (d) is, respectively, two and 12 times larger than what is shown in the figure.

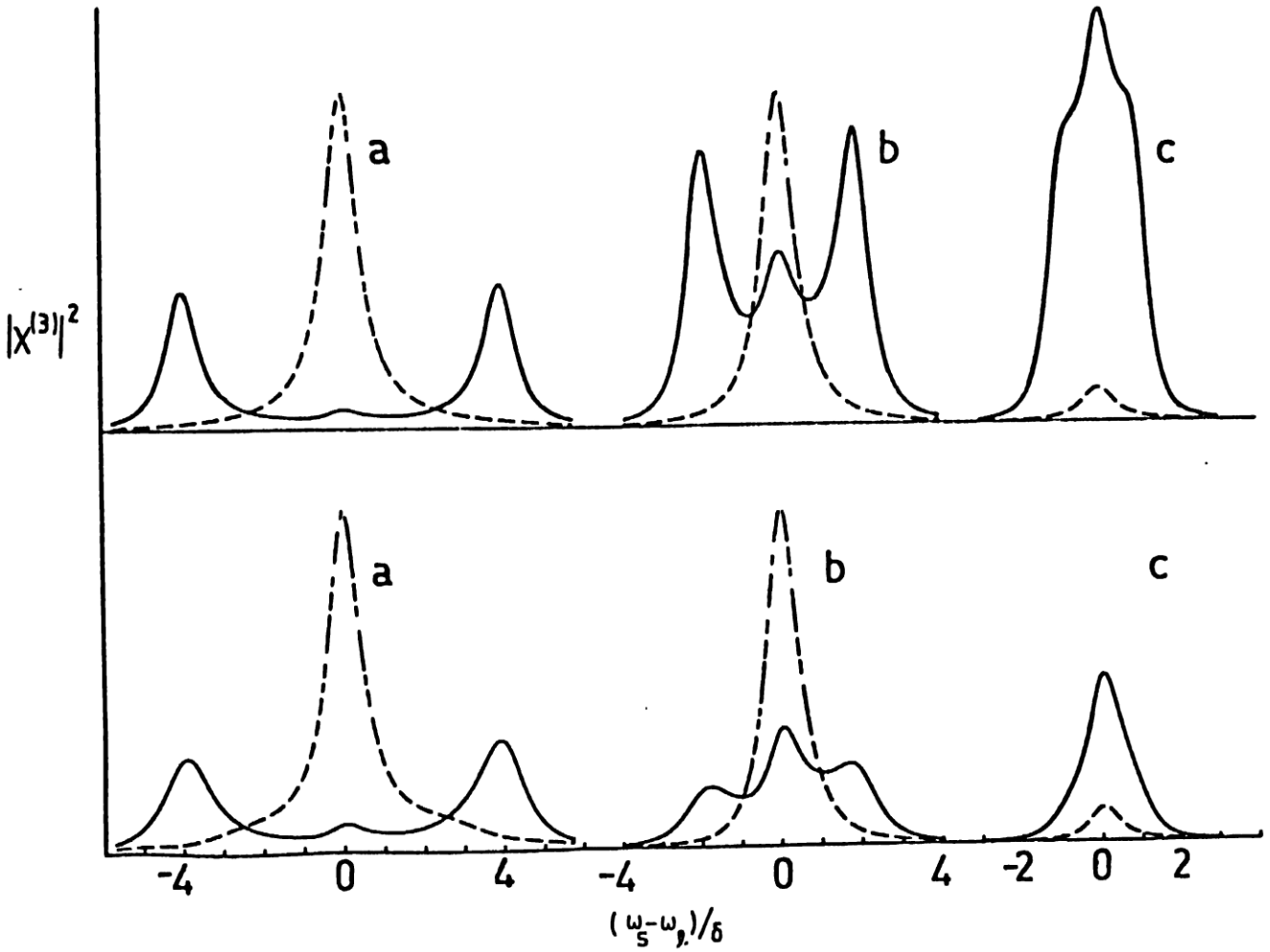


Fig.14. Same as in Fig.12 but now the case (d) dropped. The lower (upper) set of curves correspond to $\sigma/\delta=1.25$ ($\sigma/\delta=2.25$). The normalization for curves (c) is ten times larger than what is shown in the figure.

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60. Throughout this chapter (and the thesis), the term transient refers to the observation time (i.e., real time rather than some parametric time such as delay time between two fields) being less than or of the order of the typical relaxation times of the system.

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APPENDIX - 1

IMPORTANT SYMBOLS AND THEIR DEFINITIONS

We list below some of the symbols which occur frequently in the thesis and state what they stand for:

$\chi^{(n)}_{Q\{\alpha_n\}}(\{\omega_n\})$ --→ n^{th} order steady-state response of the physical observable Q

$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\})$ --→ n^{th} order steady-state susceptibility which determines the α^{th} component of the induced polarization $P^{(n)}_{\alpha}(t)$. This is a tensor of rank n+1.

d^{α}_{ij} --→ α^{th} component of the dipole matrix element $\langle i|\vec{d}|j\rangle$.

γ_{ij} --→ rate of relaxation-induced transition from state $|j\rangle$ to $|i\rangle$.

$\Gamma_{ij}^{(i\neq j)}$ --→ rate of decay of the coherence between levels $|i\rangle$ and $|j\rangle$.

Γ_{ii} --→ rate of decay of population from level $|i\rangle$ to other levels out of the system.

$\Lambda_{ij}=\omega_{ij} - i\Gamma_{ij}$ --→ complex atomic frequencies

$I\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\})$ --→ steady-state intensity-dependent susceptibility to n^{th} order in the weak fields and to all orders in the strong fields. This determines the response of the physical observable Q.

p_{ij} --→ rate of transfer of population from dressed state $|\tilde{j}\rangle$ to dressed state $|\tilde{i}\rangle$.

q_{ij} --→ rate of decay of the off-diagonal element of the density matrix in the dressed-atom picture, $\tilde{\rho}_{ij}$.

$\tilde{\Lambda}_{ij} = \beta_i-\beta_j-iq_{ij}$ --→ complex atomic frequencies of the dressed-atom.

$\chi^{(n)}_{Q\{\alpha_n\}}(\{\omega_n\},t)$ --→ n^{th} order time-dependent response of the physical observable Q.

$\chi^{(n)}_{\alpha\{\alpha_n\}}(\{\omega_n\},t)$ --→ n^{th} order time-dependent susceptibility which determines the response of the α^{th} component of the induced polarization, $P^{(n)}_{\alpha}(t)$.

Δ ---> atom-field detuning (for example, Δ_1, Δ_2, etc.)

G, g ---> atom-field coupling (for example, g_2, g_1, etc.)

$\Omega_R = \sqrt{(\Delta^2 + 4G^2)}$ ---> Rabi frequency

Ω_m ---> modulation frequency

ω ---> in general refers to optical frequencies (for example, ω_1, ω_2, etc.)

Ω, δ ---> in general refer to differences between two optical frequencies.

$\rho_{\tilde{i}\tilde{i}}^{(o)}$ ---> steady-state population of the dressed state $|\tilde{i}\rangle$.

APPENDIX - 2

List of Publications:

1. "Effects of arbitrary relaxation and strong-field dressing of energy levels on nonlinear optical susceptibilities", M. Sanjay Kumar and G.S. Agarwal, Phys. Rev. **A33**, 1817 (1986).

2. "Effects of cross relaxation and line mixing on third-order nonlinearities of resonant systems", M. Sanjay Kumar and G.S. Agarwal, Phys. Rev. **A35**, 4200 (1987).

3. "Quantum effects of the atom-cavity interaction on four-wave mixing", G.V. Varada, M. Sanjay Kumar and G.S. Agarwal, Opt. Commun. **62**, 328 (1987).

4. "Possibility of new resonances in transient nonlinear spectroscopy", M. Sanjay Kumar and G.S. Agarwal (accepted for publication in Optics Communications).

to be communicated

5. "Diagrammatic calculation of the inelastic contributions to the nonlinear susceptibilities", M. Sanjay Kumar and G.S. Agarwal.