Theory of nonlinear optical coherences in resonant degenerate four-wave mixing

Juan F. Lam and Richard L. Abrams
Hughes Research Laboratories, Malibu, California 90265
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A theory of resonantly enhanced degenerate four-wave mixing in two-level systems including the effects of atomic and photon angular momentum is presented in the absence of pump-induced saturation of the transition. It is shown that there exist three distinct quantum-mechanical amplitudes leading to the third-order polarization density. These quantum-mechanical amplitudes are shown to be sensitive to the states of polarization of the incident fields. The quantum-mechanical transport equation in the m representation is used to calculate the output signal in the various regimes of laser detuning, atomic linewidth, and polarization states of the radiation field for collinear interaction.

I. INTRODUCTION

The phenomenon of degenerate four-wave mixing (DFWM) has been a popular research subject recently due to its potential application to laser spectroscopy,[1] wave-front compensation,[2] and signal processing.[3] In the case of resonantly enhanced excitation, degenerate four-wave mixing provides a powerful tool to study the physical properties of atomic and molecular systems.[4] Pressure-broadened linewidths have been measured in both two- and three-level atomic systems.[5] Degenerate four mixing shares the same important feature with saturated absorption or two-photon spectroscopy, i.e., it yields Doppler-free spectra. Current theories have treated the atomic system as having nondegenerate energy levels, an approximation valid only for the case when the polarization state of all radiation fields are equal. In this regime, the mechanism for the generation of the signal via DFWM arises from spatial modulation of the population difference.[6] However, in general, real atoms possess angular momentum which arises, for example, from spatial symmetry of the potential energy. The effect of the existence of angular momentum leads to the violation of the assumption of nondegenerate energy levels. In this case, the relative orientation of the polarization state of the radiation fields leads to the existence of new physical mechanisms giving rise to the four-wave mixing signal.[7,8] The same mechanisms are present in the study of the Zeeman laser[9] and polarization spectroscopy.[10] The generalization of quantum levels to include magnetic degeneracies allows the possibility of studying depolarizing collision effects in resonantly enhanced degenerate four-wave mixing.[11]

We present in this paper a study of the amplitude, polarization, and spectral properties of the four-wave mixing signal generation by the nonlinear interaction of three input fields in a resonant two-level system with degenerate states. In Sec. II, we outline the approximations and model used in the description of the physics. Section III presents a qualitative picture of the fundamental physics that arise owing to the several choices of electric field polarization. Section IV presents a detailed calculation of the third-order response of the medium in the perturbation regime, i.e., the intensities of the applied and generated fields are assumed to be below saturation. Section V provides illustrative examples of the dependence of the signal on the relative orientation of the input field polarization states as well as the choice of angular momenta for the energy levels. We conclude by summarizing the main results in Sec. VI.

II. APPROXIMATION AND MODEL

We shall assume the following.

(a) The radiation field can be described in the classical picture and be written as

$$\vec{E}(\vec{r},t)=\frac{1}{2}\sum_n \hat{e}_n \mathscr{E}_n \exp i(\omega_n t-\vec{k}_n\cdot\vec{r})+\text{c.c.}\ , \tag{2.1}$$

where $\hat{e}_n$ is the unit vector describing the polarization state of the field. $\mathscr{E}_n$ is a slowly varying envelope such that

$$|\hat{k}_n\cdot\vec{\nabla}\mathscr{E}_n| \ll k_n|\mathscr{E}_n|\ . \tag{2.2}$$

ω_n and $\vec{k}_n$ are the frequency and wave vector, respectively. $\hat{k}_n$ is the unit wave vector.

(b) The atom is described by a two-level system with degenerate states (an example of which is shown in Fig. 1). The frequency difference between the upper and lower states is ω_0. The states are labeled by its total angular momentum J and z component M_j of the angular momentum.

(c) The interaction of radiation with the quantum system is described via an electric dipole coupling of the form

$$V(\vec{r},t)=-\vec{\mu}\cdot\vec{E}(\vec{r},t)\ , \tag{2.3}$$

where $\vec{\mu}$ is the electric dipole moment operator. The interaction process is near resonant so that the rotating-wave approximation is valid throughout, i.e.,

$$|\omega_n-\omega_0| \ll \omega_n+\omega_0\ . \tag{2.4}$$

(d) The lower state is populated initially by incoherent pumping processes. Relaxation processes are taken into account via effective decay rates. The spontaneous emission processes from the upper to the lower state are neglected in our description. The inclusion of such processes, which leads to optical pumping phenomena, necessitates a more elaborate description of the response of the medium as observed by Omont.[12] This work does not take into account the effects of optical pumping.

Taking these assumptions into account, the density-matrix equations which described the response of the medium to external fields are given by the following.[7]

Population:

$$\{\gamma_1+\vec{v}\cdot\vec{\nabla}\}\rho_{J_1M_1:J_1M_1}=\lambda_1(\vec{v})+\frac{1}{i\hbar}\sum_{M_2}\{V_{J_1M_1:J_2M_2}\tilde{\rho}_{J_2M_2:J_1M_1}-\tilde{\rho}_{J_1M_1:J_2M_2}V_{J_2M_2:J_1M_1}\}\ , \tag{2.5}$$

$$\{\gamma_2+\vec{v}\cdot\vec{\nabla}\}\rho_{J_2M_2:J_2M_2}=\frac{1}{i\hbar}\sum_{M_1}\{V_{J_2M_2:J_1M_1}\tilde{\rho}_{J_1M_1:J_2M_2}-\tilde{\rho}_{J_2M_2:J_1M_1}V_{J_1M_1:J_2M_2}\}\ ; \tag{2.6}$$

atomic coherences:

$$\{\gamma_{12}+i\Delta+\vec{v}\cdot\vec{\nabla}\}\tilde{\rho}_{J_1M_1:J_2M_2}=\frac{1}{i\hbar}V_{J_1M_1:J_2M_2}\{\rho_{J_2M_2:J_2M_2}-\rho_{J_1M_1:J_1M_1}\}+\frac{1}{i\hbar}\sum_{M_2'}V_{J_1M_1:J_2M_2'}\rho_{J_2M_2':J_2M_2}$$

$$-\frac{1}{i\hbar}\sum_{M_1'}\rho_{J_1M_1:J_1M_1'}V_{J_1M_1':J_2M_2}\ , \tag{2.7}$$

$$\rho_{J_2M_2:J_1M_1}=\rho^{*}_{J_1M_1:J_2M_2}\ ; \tag{2.8}$$

Zeeman coherences:

$$\{\gamma_1'+\vec{v}\cdot\vec{\nabla}\}\rho_{J_1M_1:J_1M_1'}=\frac{1}{i\hbar}\sum_{M_2}\{V_{J_1M_1:J_2M_2}\tilde{\rho}_{J_2M_2:J_1M_1'}-\tilde{\rho}_{J_1M_1:J_2M_2}V_{J_2M_2:J_1M_1'}\}\ , \tag{2.9}$$

$$\{\gamma_2'+\vec{v}\cdot\vec{\nabla}\}\rho_{J_2M_2:J_2M_2'}=\frac{1}{i\hbar}\sum_{M_1}\{V_{J_2M_2:J_1M_1}\tilde{\rho}_{J_1M_1:J_2M_2'}-\tilde{\rho}_{J_2M_2:J_1M_1}V_{J_1M_1:J_2M_2'}\}\ ; \tag{2.10}$$

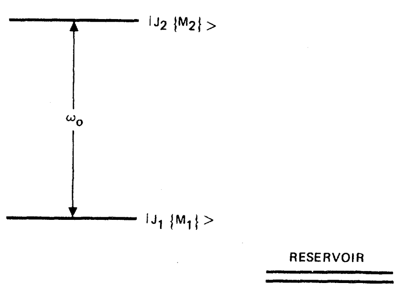

FIG. 1. Two-level system with degenerate states as a model of a resonant transition. ω_0 is the transition frequency, and J_α and M_α are the total and Z projection of the angular momentum of level α, respectively.

where $\vec{v}\cdot\vec{\nabla}$ describes the effect of atomic motion and gives rise to such effects as Doppler shifts and spatial hole burning. $\lambda_1(\vec{v})$ is the velocity-dependent incoherent pumping rate to level $|J_1\rangle$. γ_n and γ_n' are the effective decay rates of the population and Zeeman coherence, respectively. γ_{12} is the effective linewidth of the transition $|J_1\rangle\rightarrow|J_2\rangle$. $\Delta=\omega-\omega_0$ is the laser detuning from resonance. Also,

$$V_{J_1M_1:J_2M_2}=-\tfrac{1}{2}\vec{u}_{J_1M_1:J_2M_2}\cdot\sum_n\hat{e}_n\mathscr{E}_n\ , \tag{2.11}$$

$$\tilde{\rho}_{J_1M_1:J_2M_2}=\rho_{J_1M_1:J_2M_2}e^{-i\omega t}\ . \tag{2.12}$$

We have used the simplified notation that given any operator $\mathcal{D}$,

$$\mathcal{D}_{J_1M_1;J_2M_2}=\langle J_1M_1 \mid \mathcal{D} \mid J_2M_2 \rangle \tag{2.13}$$

is the matrix element of $\mathcal{D}$ between states $|J_1M_1\rangle$ and $|J_2M_2\rangle$. The set of equations (2.5)–(2.10) describe the response of the medium to external radiation fields.

The geometry of the interaction process is chosen to be collinear, i.e., the input and generated waves propagate along a line (Fig. 2). The input fields consist of the forward pump $\mathcal{E}_f$, backward pump $\mathcal{E}_b$, and the probe $\mathcal{E}_p$. The generated field is denoted by the signal $\mathcal{E}_s$. We shall be interested in those terms for which the phase of $\mathcal{E}_s$ is the complex conjugate of $\mathcal{E}_p$. One should note that in the fully collinear geometry, there are additional waves that will not be considered in this work[13] and, in principle, they can be isolated by choosing a nearly collinear geometry. Ducloy and Bloch[14] showed that the nearly collinear assumption is valid provided that $\theta < 2\gamma/ku_0$ (natural linewidth/Doppler width). For the case of sodium atoms confined to a cell at room temperature, the acceptance angle θ is 0.1°.

III. PHYSICAL PICTURE

We shall consider the physical picture of the nonlinear interaction process in both the lower and upper level of the quantum system. Each level will be characterized by its effective energy decay rate γ_J to the reservoir. The discussion to be followed is valid for any of the two energy levels.

First, consider the choice of polarization state of the radiation fields illustrated in Fig. 3. The electric dipole selection rule implies that only $\Delta M = +1$ transitions are allowed with σ_+ polarization. There exist two distinct physical contributions to the generated signal $\mathcal{E}_s$. The first one arises from a spatial modulation of the population in magnetic state $M+1$ of level $|J_2\rangle$ generated by the interference of the forward pump $\mathcal{E}_f$ and probe $\mathcal{E}_p$. The coherent scattering of the backward pump $\mathcal{E}_b$ off the spatial modulation yields a signal field $\mathcal{E}_s$ with polarization state σ_+. The second contribution arises from the spatial modulation generated by the backward pump $\mathcal{E}_b$ and probe $\mathcal{E}_p$, and the coherent scattering is performed by the forward pump $\mathcal{E}_f$. Again, the polarization state of the generated signal is identical to the forward pump, i.e., σ_+ radiation. Since both physical contributions involve the generation of population and scattering dynamics between only two magnetic states, we shall denote this type of physical mechanism as *normal population*.

Consider now the choice of polarization state illustrated in Fig. 4. There exist two additional dis-

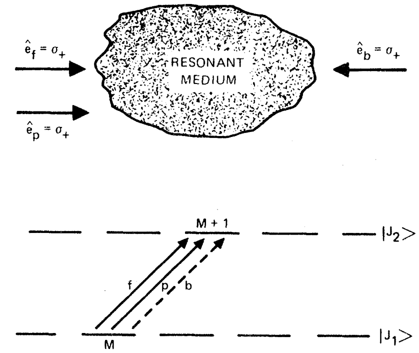

FIG. 3. Quantum-mechanical path giving rise to the normal population mechanism.

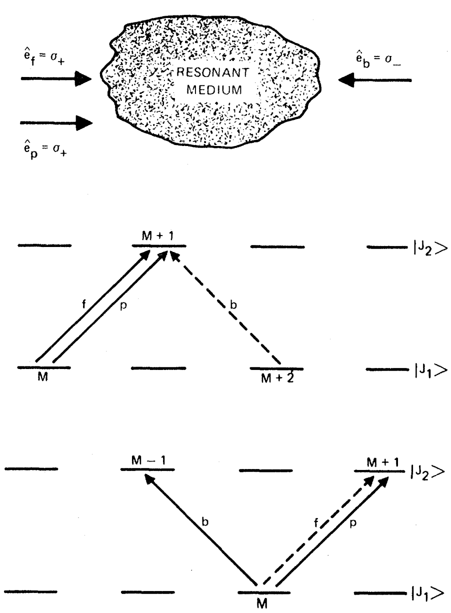

FIG. 4. Two quantum-mechanical paths giving rise to the cross-population and Zeeman-coherence mechanisms.

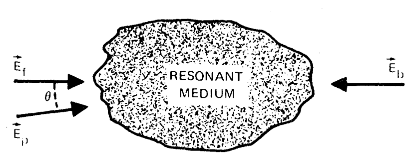

FIG. 2. Interaction geometry. $\mathcal{E}_f$ and $\mathcal{E}_b$ form a set of counterpropagating waves. Resonant medium is composed of a set of two-level systems.

tinct physical contributions. The first one arises from the generation of a spatial modulation of the population in the $M+1$ state of level $|J_2\rangle$ via the interference of the forward pump $\mathscr{E}_f$ and probe $\mathscr{E}_p$. However, the coherent scattering of the backward pump $\mathscr{E}_b$ proceeds along a different channel. It excites an optical coherence between $|J_2M+1\rangle$ and $|J_1M+2\rangle$ which generates a σ_- radiation field. Since it couples a different channel we shall denote this physical mechanism as *cross population* [Fig. 4(a)]. The second physical mechanism arises from the generation of a spatial modulation of the Zeeman coherence between $|J_2M-1\rangle$ and $|J_2M+1\rangle$ by means of the action of the backward pump $\mathscr{E}_b$ and probe $\mathscr{E}_p$. The coherent scattering of the forward pump $\mathscr{E}_f$ yields a signal whose polarization state is σ_- [Fig. 4(b)]. It should be noted that the generated signal for this case has a polarization state which is the complex conjugate of the polarization state of the probe. We shall denote this physical mechanism as *Zeeman coherence.*

In the collinear geometry, these three physical mechanisms share an important property. They yield a Doppler-free spectrum for the generated signal if the resonant medium is Doppler broadened. To understand this characteristic, let us consider the dynamics of the interaction of moving atoms with the external radiation fields. The generation of the spatial modulation of either the population or Zeeman coherence involves the excitation of the quantum system by means of the pump $\mathscr{E}_n$ $(n=f,b)$ and the probe $\mathscr{E}_p$. In the language of Doppler shifts, the resonance conditions for the generation of the spatial modulation are

$$\omega-\omega_0-\vec{k}_n\cdot\vec{v}=0\ , \tag{3.1}$$

$$\omega-\omega_0-\vec{k}_p\cdot\vec{v}=0\ . \tag{3.2}$$

The coherent scattering of the other pump wave, which generates the signal wave, yields the resonance condition

$$\omega-\omega_0+\vec{k}_p\cdot\vec{v}=0\ . \tag{3.3}$$

In writing Eq. (3.3) we used the assumption of counterpropagating pump waves, i.e., $\vec{k}_f+\vec{k}_b=0$. The velocity group that satisfies the resonance condition (3.1), (3.2), and (3.3) are those with $\vec{v}=0$. Hence the spectrum of the generated signal is a Lorentzian centered at the transition frequency ω_0 and its width is determined by the natural or collision-broadened linewidth.

IV. NONLINEAR RESPONSE OF THE MEDIUM

The medium response is determined by the polarization

$$\vec{P}(\vec{r},t)=\int_{-\infty}^{\infty}d^3v\ \mathrm{tr}[\rho(\vec{r},\vec{v},t)\vec{\mu}]\ , \tag{4.1}$$

where ρ is the density matrix satisfying the evolution equations (2.5)–(2.10) in the case of two-level systems with degenerate states, and $\vec{\mu}$ is the electric dipole moment operator. The integration over velocity takes into account the averaging over the random motion of the atoms. We shall assume that the system is in thermal equilibrium and is described by the velocity-distribution function

$$W(\vec{v})=\left[\frac{1}{\pi u_0^2}\right]^{3/2}e^{-(\vec{v}/u_0)^2}\ , \tag{4.2}$$

where $u_0=(2k_BT/m)^{1/2}$, k_B is the Boltzmann's constant, T is the equilibrium temperature, and m is the mass of the atom.

In the unsaturated regime, the polarization (4.1) is obtained by means of the perturbation solution of the density-matrix equations (2.5)–(2.10). A set of perturbation chains, which identifies the three distinct physical mechanisms discussed in Sec. III can be written in the following manner.

Normal population:

$$\rho^{(0)}_{J_1M_1:J_1M_1}\rightarrow\begin{bmatrix}\tilde{\rho}^{(1)}_{J_1M_1:J_2M_2}\\ \tilde{\rho}_{J_2M_2:J_1M_1}\end{bmatrix}\rightarrow\begin{bmatrix}\rho^{(2)}_{J_2M_2:J_2M_2}\\ \rho^{(2)}_{J_1M_1:J_1M_1}\end{bmatrix}\rightarrow\begin{bmatrix}\tilde{\rho}^{(3)}_{J_1M_1:J_2M_2}\\ \tilde{\rho}^{(3)}_{J_2M_2:J_1M_1}\end{bmatrix}\ ; \tag{4.3}$$

cross population:

$$\rho^{(0)}_{J_1M_1:J_1M_1}\rightarrow\begin{bmatrix}\tilde{\rho}^{(1)}_{J_1M_1:J_2M_2}\\ \tilde{\rho}^{(1)}_{J_2M_2:J_1M_1}\end{bmatrix}\begin{matrix}\nearrow\ \rho^{(2)}_{J_2M_2:J_2M_2}\rightarrow\begin{bmatrix}\tilde{\rho}^{(3)}_{J_1M_1':J_2M_2}\\ \tilde{\rho}^{(3)}_{J_2M_2:J_1M_1'}\end{bmatrix}\\ \searrow\ \rho^{(2)}_{J_1M_1:J_1M_1}\rightarrow\begin{bmatrix}\tilde{\rho}^{(3)}_{J_1M_1:J_2M_2'}\\ \tilde{\rho}^{(3)}_{J_2M_2':J_1M_1}\end{bmatrix}\end{matrix}\ ; \tag{4.4}$$

Zeeman coherence:

$$\rho^{(0)}_{J_1M_1:J_1M_1} \to \begin{bmatrix} \tilde{\rho}^{(1)}_{J_1M_1:J_2M_2} \\ \tilde{\rho}^{(1)}_{J_2M_2:J_1M_1} \end{bmatrix} \begin{matrix} \nearrow \rho^{(2)}_{J_2M_2':J_2M_2} \to \begin{bmatrix} \tilde{\rho}^{(3)}_{J_1M_1:J_2M_2} \\ \tilde{\rho}^{(3)}_{J_2M_2:J_1M_1} \end{bmatrix} \\ \searrow \rho^{(2)}_{J_1M_1':J_1M_1} \to \begin{bmatrix} \tilde{\rho}^{(3)}_{J_1M_1:J_2M_2} \\ \tilde{\rho}^{(3)}_{J_2M_2:J_1M_1} \end{bmatrix} \end{matrix} ; \quad (4.5)$$

where the superscript denotes the order of the perturbation parameter which is given by the Rabi frequency $\vec{\mu}\cdot\vec{E}/h$. The primed superscript indicates the case for which $M \neq M'$.

If the input radiation fields are in arbitrary polarization states, then one can decompose them in terms of σ_+ and σ_- components and apply the three basic physical contributions (4.3) to (4.5) in order to generate the nonlinear polarization (4.1). Hence, it is necessary to know the strength and spectral behavior of each physical chain.

An intuitive approach can be presented to describe the essence of the spectral behavior of the normal population, cross population, and Zeeman-coherence terms. The basic dynamics of absorption and reemission processes are necessarily the same for all three mechanisms since they are insensitive to the angular momentum of the atomic species. However, the strength of the interaction in the presence of foreign perturbers is not the same for the population (normal or cross) and Zeeman-coherence contributions. In the case of the population, no changes in the projection of the angular momentum is involved, i.e., collision effects on the population are simply visualized as an effective decay rate accompanied by changes in velocity. However, collision effects on Zeeman coherence involves the dynamics of changes of the projection of the angular momentum of the system. Hence, in general, the pressure broadening contributions to the population and Zeeman-coherence term acquire different magnitude and are reflected in part by the effective energy decay rate γ_n and Zeeman dephasing rate γ_n'.[15] In the absence of foreign perturbers, the Zeeman dephasing rate γ_n' must be given by the spontaneous-emission rate Γ which is the same as the energy decay rate in the collisionless regime.

A direct application of the perturbation chains (4.3) to (4.5) yields the following expression for the polarization contribution to the degenerate four-wave mixing signal:

$$\vec{P}(\vec{r},t)=(\vec{S}_N+\vec{S}_C+\vec{S}_Z)\mathscr{E}_f\mathscr{E}_b\mathscr{E}_p^*\exp i(\omega t+\vec{k}_p\cdot\vec{r}) , \quad (4.6)$$

where

$$\vec{S}_N=R^{(2)}_{fp}\sum_{M_1}\sum_{M_2}\vec{\mu}_{J_2M_2:J_1M_1}(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_b)(\vec{\mu}_{J_2M_2:J_1M_1}\cdot\hat{e}_p^*)(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_f)$$
$$+R^{(1)}_{fp}\sum_{M_1}\sum_{M_2}(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_f)(\vec{\mu}_{J_2M_2:J_1M_1}\cdot\hat{e}_p^*)(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_b)\vec{\mu}_{J_2M_2:J_1M_1}+(b\rightleftarrows f) \quad (4.7a)$$

is the contribution due to the normal population mechanism,

$$\vec{S}_c=R^{(2)}_{fp}\sum_{\substack{M_1,M_1'\\M_1\neq M_1'}}\sum_{M_2}\vec{\mu}_{J_2M_2:J_1M_1'}(\vec{\mu}_{J_1M_1':J_2M_2}\cdot\hat{e}_b)(\mu_{J_2M_2:J_1M_1}\cdot\hat{e}_p^*)(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_f)$$
$$+R^{(1)}_{fp}\sum_{\substack{M_2,M_2'\\M_2\neq M_2'}}\sum_{M_1}(\vec{\mu}_{J_1M_1:J_2M_2}\cdot\hat{e}_f)(\vec{\mu}_{J_2M_2:J_1M_1}\cdot\hat{e}_p^*)(\vec{\mu}_{J_1M_1:J_2M_2'}\cdot\hat{e}_b)\vec{\mu}_{J_2M_2':J_1M_1}+\{b\rightleftarrows f\} \quad (4.7b)$$

is the contribution due to the cross population mechanism, and

$$\vec{S}_Z = R_{fp}^{(2')} \sum_{M_1} \sum_{\substack{M_2, M_2' \\ M_2 \neq M_2'}} \vec{\mu}_{J_2M_2:J_1M_1} (\vec{\mu}_{J_1M_1:J_2M_2'} \cdot \hat{e}_b)(\vec{\mu}_{J_2M_2':J_1M_1} \cdot \hat{e}_p^*)(\vec{\mu}_{J_1M_1:J_2M_2} \cdot \hat{e}_f)$$
$$+ R_{fp}^{(1')} \sum_{M_2} \sum_{\substack{M_1, M_1' \\ M_1 \neq M_1'}} (\vec{\mu}_{J_1M_1:J_2M_2} \cdot \hat{e}_f)(\vec{\mu}_{J_2M_2:J_1M_1'} \cdot \hat{e}_p^*)(\vec{\mu}_{J_1M_1':J_2M_2} \cdot \hat{e}_b)\vec{\mu}_{J_2M_2:J_1M_1} + \{b \rightleftarrows f\} \quad (4.7c)$$

is the contribution due to the Zeeman-coherence mechanism.

The frequency-dependent factor $R_{np}^{(m)}$ is defined as

$$R_{np}^{(m)} = \frac{N_0}{(2i\hbar)^3} \int_{-\infty}^{\infty} d\vec{v}\, W(\vec{v}) \frac{1}{\gamma_{12} + i(\Delta + \vec{k}_p \cdot \vec{v})} \left[\frac{1}{\gamma_{12} + i(\Delta - \vec{k}_n \cdot \vec{v})} + \frac{1}{\gamma_{12} - i(\Delta - \vec{k}_p \cdot \vec{v})} \right]$$
$$\times \left[\frac{1}{\gamma_m + i(\vec{k}_p - \vec{k}_n) \cdot \vec{v}} \right], \quad n = f, b \text{ and } m = 1, 2 \quad (4.7d)$$

$$R_{np}^{(m)} \to R_{np}^{(m')} \text{ if } \gamma_m \to \gamma_m' , \quad (4.7e)$$

and for the case of collinear interaction, it reduces to the following expression:

$$R_{np}^{(m)} = \frac{1}{iku_0} \frac{N_0}{(2i\hbar)^3} \left[\frac{1}{(1+\epsilon)(\gamma_{12}+i\Delta)} \left\{ \frac{1}{\gamma_m - (1-\epsilon)(\gamma_{12}+i\Delta)} \left[Z\left[\frac{i\gamma_{12}-\Delta}{ku_0} \right] - Z\left[\frac{i\gamma_m}{(1-\epsilon)ku_0} \right] \right] \right. \right.$$
$$\left. - \frac{\epsilon}{\gamma_m + (1-\epsilon)(\gamma_{12}+i\Delta)} \left[Z\left[-\frac{i\gamma_{12}-\Delta}{ku_0} \right] - Z\left[\frac{i\gamma_m}{(1-\epsilon)ku_0} \right] \right] \right\}$$
$$- \frac{1}{2i\Delta} \left\{ \frac{1}{\gamma_m - (1-\epsilon)(\gamma_{12}+i\Delta)} \left[Z\left[\frac{i\gamma_{12}-\Delta}{ku_0} \right] - Z\left[\frac{i\gamma_m}{(1-\epsilon)ku_0} \right] \right] \right.$$
$$\left. \left. - \frac{1}{\gamma_m - (1-\epsilon)(\gamma_{12}-i\Delta)} \left[Z\left[\frac{i\gamma_{12}+\Delta}{ku_0} \right] - Z\left[\frac{i\gamma_m}{(1-\epsilon)ku_0} \right] \right] \right\} \right], \quad (4.8)$$

where $\epsilon = +1$ if $n = f$ and $\epsilon = -1$ if $n = b$. $Z(a + ib)$ is the plasma-dispersion function. Expression (4.8) is valid over all regimes of detuning and linewidth, from homogeneous to Doppler-broadened quantum systems.

Let us consider the frequency dependence of $R_{np}^{(m)}$ in the following regimes.

(a) γ_{12}, γ_m and $\Delta \gg ku_0$. These conditions are satisfied by a homogeneously broadened system, so velocity effects play no role in determining the form of $R_{np}^{(m)}$, i.e.,

$$R_{np}^{(m)} = \frac{N_0}{(2i\hbar)^3} \frac{1}{\gamma_m} \frac{2\gamma_{12}}{\gamma_{12}^2 + \Delta^2} \frac{1}{\gamma_{12} + i\Delta} . \quad (4.9)$$

(b) γ_{12} and $\Delta \gg ku_0$ but $\gamma_m < ku_0$. These conditions imply that the frequency dependence of $R_{np}^{(m)}$ will not be affected by the effect of atomic motion. However, the strength of the signal is determined by the ratio of $\gamma_m/(1-\epsilon)ku_0$. This conclusion reflects the fact that atomic motion can lead to the destruction of the spatial grating generated by the interference of $\mathscr{E}_n$ and $\mathscr{E}_p$.[16] In this case,

$$R_{np}^{(m)} = \frac{N_0}{(2i\hbar)^3} \frac{2\gamma_{12}}{\gamma_{12}^2 + \Delta^2} \frac{1}{\gamma_{12} + i\Delta}$$
$$\times \frac{1}{iku_0} Z\left[\frac{i\gamma_m}{(1-\epsilon)ku_0} \right] \quad (4.10)$$

and one can show that ratio of $R_{bp}^{(m)}$ to $R_{fp}^{(m)}$ is given by

$$\gamma_m Z\left[\frac{i\gamma_m}{2ku_0} \right] \Big/ iku_0 .$$

(c) γ_{12}, γ_m, and $\Delta \ll ku_0$. These conditions are satisfied by an extreme Doppler-broadened system. In this regime velocity effects play a substantial role in determining the frequency dependence and amplitude of $R_{np}^{(m)}$. In particular,

$$R_{fp}^{(m)} \simeq \frac{N_0}{(2i\hbar)^3} \frac{\sqrt{\pi}}{\gamma_m ku_0(\gamma_{12} + i\Delta)} \quad (4.11a)$$

and

$$R_{bp}^{(m)} \simeq \frac{N_0}{(2i\hbar)^3} \frac{\sqrt{\pi}}{(ku_0)^3} . \quad (4.11b)$$

Furthermore, the ratio of $R_{bp}^{(m)}$ to $R_{fp}^{(m)}$ at $\Delta=0$ is given by

$$\gamma_m \gamma_{12}/(ku_0)^2$$

which reflects the fact that the contribution of the spatial interference generated by $\mathscr{E}_b$ and $\mathscr{E}_p$ is negligible compared to the one generated by $\mathscr{E}_f$ and $\mathscr{E}_p$, i.e., atomic motion leads to a washout of the grating generated by $\mathscr{E}_b$ and $\mathscr{E}_p$.[17]

Now consider the properties of the polarization states $\hat{e}_s$ of the generated signal for a given set of polarization states of the input fields. In the SVEA, the evolution of $\mathscr{E}_s$ is governed by

$$\mathscr{E}_s = i\frac{\omega}{2c\epsilon_0} l \mathscr{E}_f \mathscr{E}_b \mathscr{E}_p^* \hat{e}_s^* \cdot (\vec{S}_N + \vec{S}_C + \vec{S}_Z) , \quad (4.12)$$

where l is the nonlinear interaction length. We have assumed that absorption effects are negligible (absorption coefficient multiplied by l is much less than 1). The polarization state of $\mathscr{E}_s$ depends only on the couplings of the matrix elements of the dipole moments with the polarization states radiation fields. This coupling reflects the fact that there are three distinct quantum-mechanical paths leading to the third-order polarizations as discussed in Sec. III. Furthermore, the couplings depend only on the magnitude of the angular momenta J_1 and J_2, and the dipole moment for transition. They are given by the following.

Normal population:

$$I_n = \sum_{M_1 M_2} \langle M_2 | \vec{\mu}\cdot\hat{e}_s^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_m | M_2 \rangle \langle M_2 | \vec{\mu}\cdot\hat{e}_p^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_n | M_2 \rangle ; \quad (4.13)$$

cross population:

$$I_C^{(1)} = \sum_{\substack{M_1, M_2, M_2' \\ M_2 \neq M_2'}} \langle M_1 | \vec{\mu}\cdot\hat{e}_n | M_2 \rangle \langle M_2 | \vec{\mu}\cdot\hat{e}_p^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_m | M_2' \rangle \langle M_2' | \vec{\mu}\cdot\hat{e}_s^* | M_1 \rangle , \quad (4.14a)$$

$$I_C^{(2)} = \sum_{\substack{M_2, M_1, M_1' \\ M_1 \neq M_1'}} \langle M_2 | \vec{\mu}\cdot\hat{e}_s^* | M_1' \rangle \langle M_1' | \vec{\mu}\cdot\hat{e}_m | M_2 \rangle \langle M_2 | \vec{\mu}\cdot\hat{e}_p^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_n | M_2 \rangle ; \quad (4.14b)$$

Zeeman coherence:

$$I_Z^{(1)} = \sum_{\substack{M_2, M_1, M_1' \\ M_1 \neq M_1'}} \langle M_1 | \vec{\mu}\cdot\hat{e}_n | M_2 \rangle \langle M_2 | \vec{\mu}\cdot\hat{e}_p^* | M_1' \rangle \langle M_1' | \vec{\mu}\cdot\hat{e}_m | M_2 \rangle \langle M_2 | \vec{\mu}\cdot\hat{e}_s^* | M_1 \rangle , \quad (4.15a)$$

$$I_Z^{(2)} = \sum_{\substack{M_1, M_2, M_2' \\ M_2 \neq M_2'}} \langle M_2 | \vec{\mu}\cdot\hat{e}_s^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_m | M_2' \rangle \langle M_2' | \vec{\mu}\cdot\hat{e}_p^* | M_1 \rangle \langle M_1 | \vec{\mu}\cdot\hat{e}_n | M_2 \rangle , \quad (4.15b)$$

where we have used the fact that

$$\hat{e}_s^* \cdot \vec{S}_\alpha = \sum_{n=f}^{b} \sum_{\beta=1}^{2} R_{np}^{(\beta)} I_\alpha^{(\beta)}$$

with $\alpha=N$, C, or Z and noting that $I_N^{(1)}=I_N^{(2)}=I_N$. The quantities $I_\alpha^{(\beta)}$ depend on the total angular moments J_1 and J_2 as well as the electric dipole moment of the transition. $I_\alpha^{(\beta)}$ can be calculated to yield exact analytical expressions given specific choice of input field polarization states, which will be the subject of the next section. Expression (4.12) can be rewritten as

$$\mathscr{E}_s = i\frac{\omega}{2c\epsilon_0} l \mathscr{E}_f \mathscr{E}_b \mathscr{E}_p^* \sum_\alpha \sum_{\beta=1}^{2} \sum_{n=f}^{b} R_{np}^{(\beta)} I_\alpha^{(\beta)} . \quad (4.16)$$

Equation (4.16) together with Eqs. (4.8) and (4.13)–(4.15) are the main results of this paper.

V. EXAMPLES

We shall consider several choices of the relative orientation of the radiation field polarization states for the case of optical transition $J_1=J\rightarrow J_2=J+1$. Generalization to the other cases $J_1=J\rightarrow J_2=J$ and $J_1=J+1\rightarrow J_2=J$ are straightforward and the results will not be given here. We shall decompose the polarization states in terms of the circularly polarized components

$$\sigma_+=+(\hat{x}+\hat{i}y)/\sqrt{2}$$

and

$$\sigma=(\hat{x}-\hat{i}y)/\sqrt{2}\ .$$

This representation corresponds to the choice of the quantization axis along the propagation path.

The quantities $I_\alpha^{(\beta)}$ contain a combination of four inner products of the dipole moments operator with the polarization state of the radiation fields. The decomposition into circularly polarized components together with the selection rules for electric dipole transition lead to the result that there exists only three possible components of $I_\alpha^{(\beta)}$ which are finite in magnitude. They are

$$(\vec{\mu}\cdot\sigma_\pm)(\vec{\mu}\cdot\sigma_\mp)(\vec{\mu}\cdot\sigma_\pm)(\vec{\mu}\cdot\sigma_\mp)\ ,$$

$$(\vec{\mu}\cdot\sigma_\pm)(\vec{\mu}\cdot\sigma_\mp)(\vec{\mu}\cdot\sigma_\mp)(\vec{\mu}\cdot\sigma_\pm)\ ,$$

and

$$(\vec{\mu}\cdot\sigma_\pm)(\vec{\mu}\cdot\sigma_\pm)(\vec{\mu}\cdot\sigma_\mp)(\vec{\mu}\cdot\sigma_\mp)\ .$$

In writing these terms, we have assumed, for sake of simplicity, that the $\vec{\mu}$ represents matrix elements and the order of appearance of the inner product is preserved as they are shown. The finite magnitude of these three terms results from the requirement that the initial and final quantum states for the signal generation process must be identical, i.e., the expectation value of the electric dipole moment operator is the trace of the product of the density operator and the electric dipole moment. The existence of only these three terms is consistent with the fact that the third-order susceptibility tensor in an isotropic medium has three independent components.[18] To remind the reader once more that these three terms correspond to the three quantum-mechanical amplitudes discussed above. The quantities

$$\langle J_1M_1\,|\,\vec{\mu}\,|\,J_2M_2\rangle$$

are given in terms of the reduced matrix elements and the Clebsch-Gordon coefficients.[19] The reader is referred to Ref. 19 for details of the computation.

Example 1. Consider the case where the polarization states of all the input fields are σ_+. Then the physical mechanism giving rise to the four-wave mixing signal is due to normal population. The signal field is given by

$$\mathscr{E}_s=i\frac{\omega}{2c\epsilon_0}l\mathscr{E}_f\mathscr{E}_b\mathscr{E}_p^*F(J)\sum_{\beta=1}^{2}\sum_{n=f}^{b}R_{np}^{(\beta)}\ , \tag{5.1}$$

where

$$F(J)=\tfrac{1}{4}\sum_{M=-J}^{J}|\langle J+1M-1\,|\,\mu\,|\,JM\rangle|^4\ .$$

The polarization state of the four-wave mixing signal is σ_+.

Example 2. Consider the choice of polarization states such that

$$\hat{e}_f=\sigma_+=\hat{e}_p\ \text{ and }\ \hat{e}_b=\sigma_-\ .$$

Then the mechanisms are cross population and Zeeman coherence. The signal field is given by (in the absence of foreign perturbers)

$$\mathscr{E}_s=i\frac{\omega}{2c\epsilon_0}l\mathscr{E}_f\mathscr{E}_b\mathscr{E}_p^*[G(J)(R_{fp}^{(2)}+R_{bp}^{(1)})+H(J)(R_{fp}^{(1)}+R_{bp}^{(2)})]\ ,$$

where

$$G(J)=\tfrac{1}{4}\sum_{m=-J-1}^{J+1}|\langle J+1M\,|\,\mu\,|\,JM-1\rangle|^2\times|\langle J+1M\,|\,\mu\,|\,JM+1\rangle|^2$$

and

$$H(J)=\tfrac{1}{4}\sum_{M=-J}^{J}|\langle J+1M-1\,|\,\mu\,|\,JM\rangle|^2\times|\langle J+1M+1\,|\,\mu\,|\,JM\rangle|^2\ .$$

The polarization state of the four-wave mixing signal is σ_-.

For an inhomogeneous medium in the extreme Doppler limit, the contribution due to the Zeeman coherence is negligible due to atomic washout of $R_{bp}^{(\beta)}$. Hence, it is possible to isolate the cross-population term. One can choose the case for which $\hat{e}_p=\sigma_+=\hat{e}_b$ and $\hat{e}_f=\sigma_-$ which leads to the isolation of the Zeeman coherence component in the extreme Doppler limit.

Example 3. Now consider the case for which $\hat{e}_f=\hat{x}=\hat{e}_b$ and $\hat{e}_p=\hat{y}$. For this choice all three physical mechanisms contribute to the signal field, i.e.,

$$\mathscr{E}_s=i\frac{\omega}{2c\epsilon_0}l\mathscr{E}_f\mathscr{E}_b\mathscr{E}_p^*\{[\tfrac{1}{2}G(J)-\tfrac{1}{4}L(J)+\tfrac{1}{4}M(J)](R_{fp}^{(1)}+R_{bp}^{(1)})+[\tfrac{1}{2}G'(J)-\tfrac{1}{4}L'(J)+\tfrac{1}{4}M'(J)](R_{fp}^{(2)}+R_{bp}^{(2)})\}\ ,$$

where

$$L(J)=\frac{1}{4}\sum_{M=-J-1}^{J+1}(|\langle J+1M|\mu|JM+1\rangle|^4+|\langle J+1M|\mu|JM-1\rangle|^4),$$

$$M(J)=\frac{1}{4}\sum_{M=-J-1}^{J+1}(|\langle J+1M|\mu|JM+1\rangle|^2|\langle J+1M+2|\mu|JM+1\rangle|^2$$
$$+|\langle J+1M|\mu|JM-1\rangle|^2|\langle J+1M-2|\mu|JM-1\rangle|^2).$$

The prime quantities can be obtained from the unprimed quantities by the following transformation: (1) interchange M with $M\pm1$ inside the parentheses and (2) change the summation limits from $\mp J\mp1$ to $\mp J$. Unlike the previous example where the polarization characteristics yield positive definite quantities, we can find choices of angular momenta such that $\mathscr{E}_s=0$.

One finds that for transitions $J=0\rightarrow J=1$ and $J=1\rightarrow J=1$, the three quantum-mechanical amplitudes add up to give a total cancellation of the signal.[20] This prediction has been confirmed in degenerate four-wave-mixing experiments in sodium vapor,[7] involving a single-photon excitation of the $D2$ line. The laser was tuned to the

$$3^2S_{1/2}(F=1)\rightarrow 3^2P_{3/2}(F=0)$$

transition. With the choice of polarization states of the radiation field as presented above, no signal was observed in the detector.

VI. CONCLUSION

We have presented a description of the three quantum-mechanical amplitudes or nonlinear optical coherences responsible for the signal generated in a degenerate four-wave-mixing process. The amplitudes correspond to the distinct excitation paths that a set of three arbitrarily polarized radiation fields can interact with a quantum system whose Hamiltonian is spherically symmetric. In the collinear geometry, we found that in the extreme Doppler limit the spectral response of the signal is Doppler free. This property together with the inherently high signal-to-noise[21] makes the degenerate four-wave mixing a powerful tool for the studies of atomic and molecular spectra. With the choice of polarization states such that the counterpropagating pump fields are linearly copolarized and the probe field is cross polarized, we found that the generated signal is null for electric dipole transitions $J=1\rightarrow J=0$ and $J=1\rightarrow J=1$ (in the absence of buffer gases). This effect arises from a complete cancellation of the sum of the quantum-mechanical amplitudes providing a unique approach for the studies of collisions in these transitions.[11] And last, we also showed that it is possible to isolate each of the quantum-mechanical amplitudes by an appropriate selection of the polarization states of the radiation field in the inhomogeneously broadened regime.

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