# Third-order nonlinear optical response resulting from optical pumping: Effects of atomic motion

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The formalism of Maker, Terhune, and Savage [Phys. Rev. Lett. **12**, 507 (1964)] for third-order nonlinear susceptibilities is extended to account for nonlocal response. In the case of counterpropagating beams, we show that five constants instead of two are required in general to describe the nonlinearity. In the particular case of optical pumping nonlinearities, which we study extensively, we show that four constants, which describe the magnetization and electric-quadrupole moment of the medium induced by the forward and backward beams, are sufficient. We evaluate these constants for various values of the angular momenta of the atomic levels connected by the incident field. We finally show how this formalism can be applied to several problems such as induced focusing, four-wave-mixing generation, optical instability, and polarization properties of phase-conjugate and phase-contrast mirrors.

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## I. INTRODUCTION

In 1964, Maker, Terhune, and Savage [1] showed that the third-order nonlinear polarization $\tilde{\mathbf{P}}(\mathbf{r},t)=\mathbf{P}\exp(-i\omega t)+\text{c.c.}$ induced in an isotropic medium with local response by a monochromatic optical field of the form $\tilde{\mathbf{E}}(\mathbf{r},t)=\mathbf{E}\exp(-i\omega t)+\text{c.c.}$ can in general be expressed in the form

$$\mathbf{P}=a(\mathbf{E}\cdot\mathbf{E}^*)\mathbf{E}+\tfrac{1}{2}b(\mathbf{E}\cdot\mathbf{E})\mathbf{E}^* , \tag{1}$$

where the coefficients $a$ and $b$ are parameters that characterize the nonlinear material and which can be expressed in terms of the components of the third-order optical susceptibility tensor as $a=6\chi_{1122}(\omega;\omega,\omega,-\omega)$ and $b=6\chi_{1221}(\omega;\omega,\omega,-\omega)$. Equation (1) can be derived either from explicit consideration of the symmetry properties of the nonlinear optical susceptibility tensor for an isotropic medium [1,2] or can be deduced more simply by noting that the form shown is the most general way in which three vectors **E**, **E**, and **E*** can be combined to form a new vector in a manner that is consistent with the assumed isotropy of the material system.

The goal of the present paper is to show how Eq. (1) must be modified for the more general case of a medium in which the response is not local. For instance, we consider the example illustrated in Fig. 1(a) in which counterpropagating waves described by

$$\mathbf{E}=\mathbf{E}_f e^{ikz}+\mathbf{E}_b e^{-ikz}=\mathbf{E}_f e^{i\mathbf{k}_f\cdot\mathbf{r}}+\mathbf{E}_b e^{i\mathbf{k}_b\cdot\mathbf{r}} , \tag{2}$$

with $\mathbf{k}_b=-\mathbf{k}_f$, interact in an atomic vapor. Note that the wave described by Eq. (2) displays significant spatial modulation of the electric-field amplitude on a distance scale of an optical wavelength. The response of an atomic vapor to such a field can be significantly influenced by the effects of atomic motion. For example, if an atom can move a distance of an optical wavelength in an atomic response time, the degree of atomic excitation will be determined by the spatial average of the electric-field amplitude rather than by its local value. Such effects are commonly known as grating washout effects and lead to a nonlocality in the response of the material system.

In certain special cases, such grating washout effects can be treated by a simple modification of Eq. (1). For

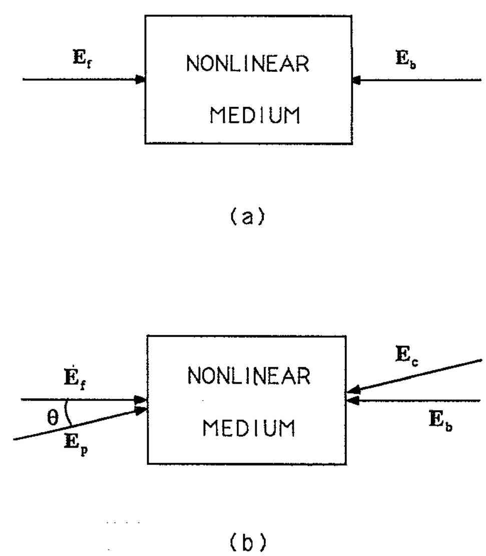


FIG. 1. (a) Nonlinear medium interacting with counterpropagating beams. The forward field $\mathbf{E}_f$ propagates along the $z$ axis and the backward field $\mathbf{E}_b$ in the opposite direction. (b) Four-wave-mixing geometry. Nonlinear medium interacting with two counterpropagating fields $\mathbf{E}_f$ and $\mathbf{E}_b$ and with two weak beams $\mathbf{E}_p$ and $\mathbf{E}_c$. The direction of propagation of $\mathbf{E}_p$ makes a small angle $\theta$ with the $z$ axis and the beam $\mathbf{E}_c$ propagates in the direction opposite to $\mathbf{E}_p$.

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example, the first term in Eq. (1) can sometimes be interpreted as describing a population grating that is written in the medium by the interference of $\mathbf{E}$ with $\mathbf{E}^*$ and which is read out by the scattering of $\mathbf{E}$ from this grating. Such a contribution would be expected to be strongly diminished by grating washout effects, and these effects can be modeled by multiplying the coefficient $a$ of Eq. (1) by a grating washout factor $\eta$, where $|\eta|<1$, for those contributions to $\mathbf{E}\cdot\mathbf{E}^*$ that display significant spatial modulation. On the other hand, the second term in Eq. (1) can sometimes be interpreted as describing a spatially invariant two-photon coherence described by the product $\mathbf{E}\cdot\mathbf{E}$, which is probed by an emission process described by $\mathbf{E}^*$. Such a contribution would not be expected to be influenced by grating washout effects. In general, however, as we show below, the preceding physical interpretations of the two components of Eq. (1) are not correct, the effects of motion cannot be described so simply and an expression more general than Eq. (1) must be employed to describe the nonlinear interaction.

## II. NONLINEAR POLARIZATION

### A. General expression

Most generally, the nonlinear polarization at frequency $\omega$ produced by an optical field of the form (2) can be represented as

$$\mathbf{P}=\mathbf{P}_f e^{ikz}+\mathbf{P}_b e^{-ikz}=\mathbf{P}_f e^{i\mathbf{k}_f\cdot\mathbf{r}}+\mathbf{P}_b e^{i\mathbf{k}_b\cdot\mathbf{r}} , \tag{3}$$

where $\mathbf{P}_f$ is given by the expression

$$\mathbf{P}_f=a_1(\mathbf{E}_f\cdot\mathbf{E}_f^*)\mathbf{E}_f+a_2(\mathbf{E}_b\cdot\mathbf{E}_b^*)\mathbf{E}_f+a_3(\mathbf{E}_f\cdot\mathbf{E}_b^*)\mathbf{E}_b +\tfrac{1}{2}b_1(\mathbf{E}_f\cdot\mathbf{E}_f)\mathbf{E}_f^*+b_2(\mathbf{E}_b\cdot\mathbf{E}_f)\mathbf{E}_b^* \tag{4}$$

and where $\mathbf{P}_b$ is given by an analogous expression obtained by interchanging subscripts $f$ and $b$ everywhere. The factor of $\frac{1}{2}$ is included in the fourth but not the fifth terms in Eq. (4) for later convenience. The form of Eq. (4) follows from the fact that the five displayed terms are the only third-order combinations of the vectors $\mathbf{E}_f$, $\mathbf{E}_f^*$, $\mathbf{E}_b$, $\mathbf{E}_b^*$ that represent a response having frequency $\omega$ (i.e., containing a positive-frequency field amplitude twice and the complex conjugate of a positive-frequency field amplitude once) and having wave vector $\mathbf{k}_f$.

In the limit in which grating washout effects are negligible, the predictions of the formalism [Eqs. (3) and (4)] must reduce to those of the standard expression (1) with $\mathbf{E}$ given by expression (2). From this requirement we deduce that in the absence of grating washout effects the coefficients in our expression are related to those of the standard form (1) by

$$a_1=a_2=a_3=a , \quad b_1=b_2=b . \tag{5}$$

Of course, in general the five coefficients $a_1$, $a_2$, $a_3$, $b_1$, and $b_2$ are expected to be distinct and their values must be determined either by experiment or by explicit calculation involving consideration of the physical mechanism leading to a nonlinear response and to the effects of atomic motion.

### B. Relation with the components of the third-order nonlinear susceptibility tensor

From a formal point of view, the coefficients $a_1$, $a_2$, $a_3$, $b_1$, and $b_2$ can be related to the components of a generalized nonlinear susceptibility tensor defined so as to depend functionally upon both the frequencies and wave vectors of the interacting waves. This tensor is defined such that the frequency and wave-vector-dependent polarization is related to the frequency and wave-vector-dependent electric-field amplitude according to

$$P_i(\omega,\mathbf{k})=\sum_{j,k,l}\sum_{m,n,o}\chi_{ijkl}(\omega,\mathbf{k};\omega_m\mathbf{k}_m,\omega_n\mathbf{k}_n,\omega_o\mathbf{k}_o) \times E_j(\omega_m\mathbf{k}_m)E_k(\omega_n\mathbf{k}_n)E_l(\omega_o\mathbf{k}_o) , \tag{6}$$

where it is to be understood that in performing the summation over $m$, $n$, and $o$ only those terms are to be retained for which $\omega=\omega_m+\omega_n+\omega_o$ and $\mathbf{k}=\mathbf{k}_m+\mathbf{k}_n+\mathbf{k}_o$. Let us now determine the independent components of this tensor that are needed to describe the nonlinear interaction shown in Fig 1(a). We first note that even with the frequencies $(\omega_m,\omega_n,\omega_o)$ arbitrarily taken in the order $(\omega,\omega,-\omega)$, there are still three ways in which the wave vectors can sum to $\mathbf{k}_f$, namely,

$$\mathbf{k}_f=\mathbf{k}_f+\mathbf{k}_f-\mathbf{k}_f , \quad \mathbf{k}_f=\mathbf{k}_f+\mathbf{k}_b-\mathbf{k}_b , \quad \mathbf{k}_f=\mathbf{k}_b+\mathbf{k}_f-\mathbf{k}_b . \tag{7}$$

Each of these three wave-vector orderings can occur with each of the three independent Cartesian components of the susceptibility tensor, namely,

$$\chi_{1122} , \quad \chi_{1212} , \quad \chi_{1221} . \tag{8}$$

However, because the nonlinear susceptibility must possess intrinsic permutation symmetry, not all nine of these quantities are independent. For example, it is clear that $\chi_{1122}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_b,-\omega-\mathbf{k}_b)$ must be equal to $\chi_{1212}(\omega\mathbf{k}_f;\omega\mathbf{k}_b,\omega\mathbf{k}_f,-\omega-\mathbf{k}_b)$ since these two quantities are related by the interchange of dummy variables, namely, the simultaneous interchange of the Cartesian indices, frequencies, and wave vectors of the second and third fields. By applying such arguments systematically, one finds that there are in fact five independent components of the susceptibility [they are listed in Eq. (9) below]. Finally, these susceptibility components are related to the parameters appearing in Eq. (4) by requiring that $\mathbf{P}(\omega,\mathbf{k}_f)$ of Eq. (6) must equal $\mathbf{P}_f$ of Eq. (4). We thereby find that

$$\begin{aligned}
a_1&=6\chi_{1122}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_f,-\omega-\mathbf{k}_f)\\
&=6\chi_{1212}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_f,-\omega-\mathbf{k}_f) ,\\
a_2&=6\chi_{1122}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_b,-\omega-\mathbf{k}_b)\\
&=6\chi_{1212}(\omega\mathbf{k}_f;\omega\mathbf{k}_b,\omega\mathbf{k}_f,-\omega-\mathbf{k}_b) ,\\
a_3&=6\chi_{1122}(\omega\mathbf{k}_f;\omega\mathbf{k}_b,\omega\mathbf{k}_f,-\omega-\mathbf{k}_b)\\
&=6\chi_{1212}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_b,-\omega-\mathbf{k}_b) ,\\
b_1&=6\chi_{1221}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_f,-\omega-\mathbf{k}_f) ,\\
b_2&=6\chi_{1221}(\omega\mathbf{k}_f;\omega\mathbf{k}_f,\omega\mathbf{k}_b,-\omega-\mathbf{k}_b)\\
&=6\chi_{1221}(\omega\mathbf{k}_f;\omega\mathbf{k}_b,\omega\mathbf{k}_f,-\omega-\mathbf{k}_b) .
\end{aligned} \tag{9}$$

Equation (9) establishes the relation between the parameters $a_i$ and $b_i$ that appear in Eq. (4) and the components of the nonlinear optical susceptibility tensor.

The form of expression (4) shows that in general five parameters are needed to describe the nonlinear polarization induced in a nonlinear medium by counterpropagating waves. Under special circumstances, not all five of these parameters are independent. For example, when grating washout effects are unimportant, as in the case of highly nonresonant electronic nonlinearities, only two of these parameters are independent. Moreover, Saikan [3] has shown that the near-resonant electronic response of a Doppler-broadened atomic transition connecting two excited levels (within the Lamb model) can be described by three independent components of the nonlinear optical susceptibility.

### C. Effective linear susceptibility

For computational convenience, it is often useful to be able to describe the nonlinear polarization in terms of an effective linear susceptibility. For example, the nonlinear polarization influencing the forward-going wave can be represented as

$$P_{fi}=\sum_j(\chi_{ij}^{(0)}E_{fj}+\chi_{ij}^{(2k)}E_{bj}) , \tag{10}$$

where $\chi_{ij}^{(0)}$ describes the spatially uniform part of the effective linear susceptibility and where $\chi_{ij}^{(2k)}$ describes the part of the effective linear susceptibility associated with a spatial dependence of $\exp(2ikz)$.

We find that Eq. (10) leads to prediction identical to those of Eq. (4) if these two quantities are equal to

$$\chi_{ij}^{(0)}=\left[\left[a_1-\frac{b_1}{2}\right](\mathbf{E}_f\cdot\mathbf{E}_f^*)+(a_2-b_2)(\mathbf{E}_b\cdot\mathbf{E}_b^*)\right]\delta_{ij}+\frac{b_1}{2}(E_{fi}E_{fj}^*+E_{fj}E_{fi}^*) \tag{11a}$$

and

$$\chi_{ij}^{(2k)}=a_3(\mathbf{E}_f\cdot\mathbf{E}_b^*)\delta_{ij}+b_2(E_{fi}E_{bj}^*+E_{fj}E_{bi}^*) . \tag{11b}$$

Note, however, that the decomposition of $P_{fi}$ into the two terms shown in Eq. (10) *is not unique* and in fact the value of $P_{fi}$ is left unchanged if the expressions for $\chi_{ij}^{(0)}$ and $\chi_{ij}^{(2k)}$ are modified according to

$$\chi_{ij}^{(0)}\rightarrow\chi_{ij}^{(0)}+c(\mathbf{E}_b\cdot\mathbf{E}_b^*)\delta_{ij} , \tag{12a}$$

$$\chi_{ij}^{(2k)}\rightarrow\chi_{ij}^{(2k)}-cE_{fi}E_{bj}^* , \tag{12b}$$

where $c$ is any complex number.

Even though there is no unique form for the quantities $\chi_{ij}^{(0)}$ and $\chi_{ij}^{(2k)}$ of Eq. (10), *there may be particular forms for these quantities which more naturally reflect the physical meaning of these quantities.* For example, one may require that the expression of $\chi_{ij}^{(0)}$, which describes the spatially uniform part of the susceptibility, be independent of grating washout coefficients [4].

## III. OPTICAL PUMPING NONLINEARITIES

In the remainder of the present paper, we present a theoretical treatment of the tensor properties of the third-order nonlinear optical response of an atomic vapor resulting from optical pumping (i.e., caused by the redistribution of population among the Zeeman sublevels of the ground state induced by the incident beams). We chose to study this type of nonlinearity both because it can lead to a very large nonlinear optical response and because it is strongly influenced by grating washout effects. Both of these properties result from the fact that the response times for optical pumping tend to be quite long (microseconds to milliseconds). Optical pumping nonlinearities are known to lead to optical phase conjugation with high reflectivity [5], to bistability [6], instabilities, and chaos [7] in interacting laser beams. While there have been previous treatments that deal with the tensor properties of optical pumping nonlinearities in special cases [8], our treatment generalizes this previous work by allowing the upper and lower electronic levels to possess arbitrary angular momentum quantum numbers ($J$) and by considering counterpropagating beams. Our approach also differs from Saikan's theory [3] because we discuss the case of a closed system where the lower state is the ground state while Saikan considers an open system where the lower state is an excited state. Furthermore, while the model of Saikan describes optical pumping due to absorption (Dehmelt-type optical pumping), our approach includes both absorption and transfer of excited-state observables by spontaneous emission (Kastler-type optical pumping).

### A. Components of the nonlinear polarization

The details of the calculations are presented in the Appendix. Here we simply quote the results. We find that the amplitude of the nonlinear polarization influencing the forward-going wave is given by an expression having the form of Eq. (4) with

$$\begin{aligned} a_1&=(-\tfrac{1}{2}\chi_1^s+\tfrac{1}{6}\chi_2^s) ,\\ a_2&=-\frac{\chi_2^c}{3} ,\\ a_3&=-\tfrac{1}{2}(\chi_1^c-\chi_2^c) ,\\ b_1&=(\chi_1^s+\chi_2^s) ,\\ b_2&=\tfrac{1}{2}(\chi_1^c+\chi_2^c) , \end{aligned} \tag{13}$$

where $\chi_1^s$ and $\chi_1^c$ respectively correspond to the nonlinear response resulting from the induced magnetization of the ground-state orientation by the field $E_f$ (self-action) and the field $E_b$ (cross action). Similarly $\chi_2^s$ and $\chi_2^c$ describe the nonlinear response resulting from the induced quadrupole moment of the ground state (alignment) due to the forward and backward fields, respectively.

A better insight into the tensorial properties of the polarization $\mathbf{P}_f$ can be obtained by writing Eq. (4) as

$$\mathbf{P}_f=\frac{\chi_1^s}{2}\mathbf{E}_f\times(\mathbf{E}_f^*\times\mathbf{E}_f)+\frac{\chi_1^s}{2}\mathbf{E}_f\times(\mathbf{E}_b^*\times\mathbf{E}_b)$$
$$-\frac{\chi_2^s}{3}\mathbf{E}_f(\mathbf{E}_f^*\cdot\mathbf{E}_f)-\frac{\chi_2^c}{3}\mathbf{E}_f(\mathbf{E}_b^*\cdot\mathbf{E}_b)$$
$$+\frac{\chi_2^s}{2}\mathbf{E}_f\cdot(\mathbf{E}_f^* * \mathbf{E}_f)+\frac{\chi_2^c}{2}\mathbf{E}_f\cdot(\mathbf{E}_b^* * \mathbf{E}_b)\ , \qquad (14)$$

where we have set $\mathbf{A}\cdot(\mathbf{B}*\mathbf{C})=(\mathbf{A}\cdot\mathbf{B})\mathbf{C}+(\mathbf{A}\cdot\mathbf{C})\mathbf{B}$.

### B. Detailed expression of the four optical pumping coefficients

The coefficients $\chi_1^s$, $\chi_1^c$, $\chi_2^s$, and $\chi_2^c$ are given by

$$\chi_j^s=g_jF^s(\delta)\ , \qquad (15a)$$

$$\chi_j^c=g_jF^c(\delta)\ , \qquad (15b)$$

with

$$g_j=-\frac{ND^4}{\hbar^3}\frac{1}{2J_g+1}\frac{\Gamma}{\gamma_j}B_j\overline{B}_j\ , \qquad (15c)$$

$$F^s(\delta)=\int dv_z\,W(v_z)\frac{1}{\left[(\delta-kv_z)^2+\frac{\Gamma^2}{4}\right]}\frac{1}{(\delta-kv_z)+i\frac{\Gamma}{2}}\ , \qquad (15d)$$

$$F^c(\delta)=\int dv_z\,W(v_z)\frac{1}{\left[(\delta+kv_z)^2+\frac{\Gamma^2}{4}\right]}\frac{1}{(\delta-kv_z)+i\frac{\Gamma}{2}}\ ; \qquad (15e)$$

Here $N$ is the number density of atoms, $D$ is the reduced matrix element of the dipole moment operator defined by Eq. (A9) of the Appendix, $\Gamma$ is the spontaneous emission population decay rate of the upper level. $\gamma_1$ is the relaxation rate of atomic magnetization, $\gamma_2$ (which is often approximately equal to $\gamma_1$) is the relaxation rate of the ground-state quadrupole moment, and $\delta=\omega-\omega_o$ is the detuning from resonance. The quantities $B_j$ and $\overline{B_j}$ are given by the expressions

$$B_j(J_g,J_e)=(-1)^{j+1+J_g+J_e}\begin{Bmatrix}1 & 1 & j\\ J_g & J_g & J_e\end{Bmatrix} \qquad (16a)$$

and

$$\overline{B}_j(J_g,J_e)=(-1)^{j+1}\left[B_j(J_g,J_e)+(-1)^{J_g+J_e}(2J_e+1)\begin{Bmatrix}J_e & J_e & j\\ J_g & J_g & 1\end{Bmatrix}B_j(J_e,J_g)\right]\ , \qquad (16b)$$

where $J_g$ and $J_e$ represent the angular momentum quantum numbers of the ground and excited states, respectively, and { } represents the $6j$ symbol. In Table I, the quantity $C_j=B_j\overline{B}_j$ is listed for several different values of $J_g$ and $J_e$.

In formulas (15d) and (15e) $W(v_z)$ describes the normalized velocity distribution. If we assume a Maxwell-Boltzmann distribution

TABLE I. $C_k=B_k\overline{B}_k$ coefficients versus angular momenta of the ground ($J_g$) and excited ($J_e$) levels.

| Transition | $C_1$ | $C_2$ |
|---|---|---|
| $J_g=\frac{1}{2}\to J_e=\frac{1}{2}$ | $\frac{2}{27}$ | 0 |
| $J_g=\frac{1}{2}\to J_e=\frac{3}{2}$ | $-\frac{1}{54}$ | 0 |
| $J_g=1\to J_e=0$ | $\frac{1}{9}$ | $-\frac{1}{9}$ |
| $J_g=1\to J_e=1$ | $\frac{1}{24}$ | $-\frac{1}{24}$ |
| $J_g=1\to J_e=2$ | $-\frac{1}{72}$ | $\frac{1}{360}$ |
| $J_g=2\to J_e=1$ | $\frac{1}{40}$ | $-\frac{21}{1000}$ |
| $J_g=2\to J_e=2$ | $\frac{11}{1080}$ | $-\frac{7}{600}$ |
| $J_g=2\to J_e=3$ | $-\frac{1}{135}$ | $\frac{1}{375}$ |
| $J_g=3\to J_e=2$ | $\frac{2}{189}$ | $-\frac{1}{5}\sqrt{\frac{4}{2401}}$ |
| $J_g=3\to J_e=3$ | $\frac{23}{27\sqrt{56\times 896}}$ | $\frac{-1}{\sqrt{56\times 896}}$ |
| $J_g=3\to J_e=4$ | $\frac{-1}{\sqrt{56\times 896}}$ | $\frac{3}{\sqrt{56\times 43904}}$ |

$$W(v_z)=\frac{1}{u\sqrt{\pi}}\exp-\frac{v_z^2}{u^2} \qquad (17)$$

with $u=\sqrt{2k_BT/m}$, two limits are of particular interest depending on the relative values of the Doppler width $ku$ and of the detuning $\delta=\omega-\omega_0$.

(i) Detuning larger than the Doppler width ($|\delta|\gg ku$). In this limit, formulas (15d) and (15e) yield

$$F^{(s)}(\delta)=F^{(c)}(\delta)\approx\frac{1}{\delta^3}\ . \qquad (18)$$

It can also be noticed that the effect are purely dispersive in this range of detunings. Note also that even in this domain where $\mathbf{P}_f$ only depends on two parameters (because $\chi_j^s=\chi_j^c$), there is no possibility to write $\mathbf{P}_f$ in a form similar to Eq. (1) because the relation (5) is not satisfied.

(ii) Detuning smaller than the Doppler width ($|\delta|\ll ku$). In this limit a contour integration in the complex plane gives

$$F^{(s)}(\delta)=-\frac{2i\sqrt{\pi}}{\Gamma^2(ku)}\ , \qquad (19a)$$

$$F^{(c)}(\delta)=+\frac{\sqrt{\pi}}{\Gamma(ku)\left[\delta+i\frac{\Gamma}{2}\right]}\ . \qquad (19b)$$

The cross term thus displays a resonance for $\delta \approx 0$ while the self-term remains constant for detuning smaller than the Doppler width. Note also that the effect is now mostly absorptive.

The range of validity of the present approach is limited by the condition $s \ll \gamma_j/\Gamma \ll 1$ where $s$ is the saturation parameter $[s = D^2(I_f + I_b)/\hbar^2(\delta^2 + \Gamma^2/4)]$.

We also assume $\Gamma/ku \ll 1$ so that almost complete grating washout is achieved. When the grating induced by the counterpropagating beams is not completely destroyed by atomic motion, additional terms proportional to grating washout factors $\eta_j$ should be added. The coefficients $\eta_j$ are on the order of $\gamma_j/ku$. In most cases, they are very small ($<10^{-3}$) and can be replace by 0. In fact, we neglect also in the calculation terms arising from saturation of electronic nonlinearities (or from light-shift effects) that are smaller than the optical pumping nonlinearities (by a factor on the order of $\gamma_k/\Gamma$) but generally larger than the product of these optical pumping nonlinearities by $\eta_j$.

### C. Effective linear susceptibility

We have shown in Sec. II C that the form for the quantities $\chi_{ij}^{(0)}$ and $\chi_{ij}^{(2k)}$ of Eq. (10) is not unique. Nevertheless there exists certain forms for these quantities which are more natural. For example, for optical nonlinearities resulting from optical pumping, these quantities can be expressed as

$$\chi_{ij}^{(0)} = \frac{\chi_1^s}{2}[E_{fi}^* E_{fj} - E_{fi} E_{fj}^*] + \frac{\chi_2^s}{2}[E_{fi}^* E_{fj} + E_{fi} E_{fj}^*] - \frac{\chi_2^s}{3}(\mathbf{E}_f \cdot \mathbf{E}_f^*)\delta_{ij} + \frac{\chi_1^c}{2}[E_{bi}^* E_{bj} - E_{bi} E_{bj}^*] + \frac{\chi_2^c}{2}[E_{bi}^* E_{bj} + E_{bi} E_{bj}^*] - \frac{\chi_2^c}{3}(\mathbf{E}_b \cdot \mathbf{E}_b^*)\delta_{ij} \quad (20)$$

and

$$\chi_{ij}^{(2k)} = 0 \; . \quad (21)$$

This last equation should be understood as a natural consequence of the complete destruction of the short-period grating by atomic motion.

## IV. APPLICATIONS

We now present applications of the preceding formalism to several interesting physical problems: self- and induced focusing, phase-conjugate and phase-contrast mirrors, and optical instabilities.

### A. Counterpropagating beams

We begin by considering two counterpropagating beams $\mathbf{E}_f$ and $\mathbf{E}_b$. For the principal polarizations considered below (beams linearly polarized along the $x$ or $y$ direction or having a circular polarization $\sigma^+$ or $\sigma^-$), the atomic polarization $\mathbf{P}_f$ and the forward wave $\mathbf{E}_f$ have the same polarization. The amplitude $P_f$ can be expanded into two components proportional to $|E_f|^2 E_f$ and $|E_b|^2 E_f$ whose coefficients depend on the beam polarization. The values of these coefficients are given in Table II in terms of the five coefficients $a_i$ and $b_i$ introduced in Eq. (4). For the case of optical pumping nonlinearities, analogous results are obtained in terms of the quantities $\chi_j^s$ and $\chi_j^c$ in Table III. The first column of Tables II and III describes self-action of a traveling wave whereas the second column describes the effect induced by the counterpropagating wave.

We first consider *self-action* of a *linearly polarized wave*. The only optical pumping coefficient relevant for this discussion is $\chi_2^s$ as can be seen in Table III. This result originates from the fact that a linearly polarized beam creates only alignment in the lower level. The beam will experience self-defocusing when $\chi_2^s < 0$ and self-focusing when $\chi_2^s > 0$. According to Eqs. (15a) and (18), the sign of $\chi_2$ for large $|\delta|$ is determined by the signs of $\delta$ (detuning) and $C_2 = B_2\bar{B}_2$. Table I shows that $C_2$ is negative for $J_g \to J_g$ and $J_g \to J_g - 1$ transitions whereas it is positive for $J_g \to J_g + 1$ transitions. We deduce from this result that optical pumping nonlinearities tend to induce *self-defocusing* below resonance for $J_g \to J_g$ and $J_g \to J_g - 1$ transitions while it induces *self-focusing* for $J_g \to J_g + 1$ transitions. We note that in this last case, the effect of optical pumping is *opposite* to the well-known effect of atomic saturation which leads to self-defocusing below resonance. To understand this point, we can, for example, consider the $J_g = 1 \to J_e = 2$ transition (Fig. 2) and a $\pi$-polarized beam. Optical pumping tends to cause more atoms to accumulate in the $m = 0$ Zeeman sublevel than in the $m = \pm 1$ sublevels. This leads to a larger value of the susceptibility because the Clebsch-Gordan coefficient connecting the $m = 0$ sublevels is larger than the Clebsch-Gordan coefficients for $m_g = -1 \to m_e = -1$ and $m_g = 1 \to m_e = 1$ transitions.

We now consider *self-action* in the case of a *circularly polarized* beam. Because circular polarization generally creates both orientation $\chi_1^s$ and alignment $\chi_2^s$, the condition for self-focusing or self-defocusing depends upon some combination of these quantities (see Table III). Here again, optical pumping can have the same effect or an effect opposite to that of atomic saturation. For example, we discuss the simple case of transitions starting from $J_g = \frac{1}{2}$ (for which $\chi_2^s = 0$). In the case of $J_g = \frac{1}{2} \to J_e = \frac{1}{2}$ transitions, optical pumping and atomic saturation both tend to induce self-defocusing below resonance while for a $J_g = \frac{1}{2} \to J_e = \frac{3}{2}$ transition, optical pumping and atomic saturation have opposite effects. If

TABLE II. Expansion of the forward polarization $P_{fb}$ into two terms, respectively proportional to $|\mathbf{E}_f|^2 E_f$ and $|\mathbf{E}_b|^2 E_f$, for various polarizations $\mathbf{e}_f$ and $\mathbf{e}_b$. Proportionality coefficients are given in terms of the coefficients $a_1$, $a_2$, $a_3$, $b_1$, and $b_2$.

| Coefficient of $P_{fb}$ | $\lvert E_f\rvert^2 E_f$ | $\lvert E_b\rvert^2 E_f$ |
|---|---|---|
| $P_{xx} = P_{yy}$ | $a_1 + \frac{1}{2}b_1$ | $a_2 + a_3 + b_2$ |
| $P_{xy} = P_{yx}$ | $a_1 + \frac{1}{2}b_1$ | $a_2$ |
| $P_{++} = P_{--}$ | $a_1$ | $a_2 + a_3$ |
| $P_{+-} = P_{-+}$ | $a_1$ | $a_2 + b_2$ |

TABLE III. Expansion of the forward polarization $P_{fb}$ into two terms, respectively proportional to $|\mathbf{E}_f|^2 E_f$ and to $|\mathbf{E}_b|^2 E_f$, for different polarizations $\mathbf{e}_f$ and $\mathbf{e}_b$. Proportionality coefficients are given in terms of the coefficients $\chi_1^s$, $\chi_1^c$, $\chi_2^s$, and $\chi_2^c$.

| Coefficient of $P_{fb}$ | $\lvert E_f\rvert^2 E_f$ | $\lvert E_b\rvert^2 E_f$ |
|---|---|---|
| $P_{xx}$ | $\frac{2}{3}\chi_2^s$ | $\frac{2}{3}\chi_2^c$ |
| $P_{xy}$ | $\frac{2}{3}\chi_2^s$ | $-\frac{1}{3}\chi_2^c$ |
| $P_{++}$ | $\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $-\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ |
| $P_{+-}$ | $-\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ |

optical pumping is the dominant nonlinear effect one should in this case observe self-focusing below resonance and self-defocusing above.

We now study the case of *induced focusing* caused by an intense *counterpropagating* beam. In the limit ($E_f \ll E_b$) and assuming similar transverse dimensions for the two beams, the focusing of $E_f$ will be determined by the coefficients of the second column of Tables II and III. From the relative signs of the coefficients of $|E_b|^2 E_f$ in the two first lines of Table III, we immediately deduced that the effect induced by an $x$-polarized beam is just opposite to the effect induced by a $y$-polarized beam. If an $x$-polarized beam induces focusing, a $y$-polarized beam induces defocusing and vice versa. Similar effects occur for circular polarization. For example, for transitions starting from $J_g=\frac{1}{2}$ (where $\chi_2^c=0$), one can switch from induced focusing to induced defocusing by changing the polarization $\sigma_+$ of the counterpropagating beam into its opposite $\sigma_-$ (see third and four lines of column 2 of Table III).

### B. Four-wave-mixing geometry

We now consider four-wave mixing interactions. We introduce a probe beam $\mathbf{E}_p$ whose direction of propagation makes a small angle $\theta$ with respect to the direction of propagation of the forward beam [Fig. 1(b)]. The beam propagating in the $+z$ direction can then be written as

$$[\mathbf{E}_f+\mathbf{E}_p\exp(i\mathbf{K}\cdot\mathbf{r})]\exp(i\mathbf{k}_f\cdot\mathbf{r}) ,$$

where $\mathbf{K}$ lies in a plane orthogonal to $\mathbf{k}_f$. The magnitude of $K\approx k\theta$ is assumed to be sufficiently small that any residual Doppler effect due to atomic motion in the $xy$ plane can be neglected. The interaction of the fields $\mathbf{E}_f$, $\mathbf{E}_b$, and $\mathbf{E}_p$ in the nonlinear medium induces the generation of a conjugate beam $\mathbf{E}_c$ [9] so that the field propagating in the $-z$ direction can be written as

$$[\mathbf{E}_b+\mathbf{E}_c\exp(-i\mathbf{K}\cdot\mathbf{r})]\exp(i\mathbf{k}_b\cdot\mathbf{r}) .$$

The amplitudes $E_p$ and $E_c$ of the new fields are assumed to be much smaller than the amplitudes of the pump fields $E_f$ and $E_b$. The following calculation will thus be limited to *first order* in $E_p$ and $E_c$. The terms that involve only the fields $E_f$ and $E_b$ are identical to those shown in Tables II and III. We now consider the new terms which can be separated into five components (Tables IV and V). First there are terms proportional to $|E_f|^2E_p$ and $|E_b|^2E_p$ which describe the influence of the forward pump beam and of the backward pump beam on the nonlinear index of the probe field. We see that the influence of the backward pump on the probe is identical to the effect of the backward pump on the forward pump (see Tables II and III) as expected. Terms such as $|E_f|^2E_p$ are interesting for several problems. For example, such terms describe *induced focusing* and show that the effect of a *copropagating* beam may be different from the effect of a *counterpropagating* beam. Consider, for example, a probe beam polarized along the $y$ direction and a pump beam polarized along the $x$ direction. If the pump beam is counterpropagating, the relevant parameter is $-\chi_2^c/3$ while the corresponding parameter is $-\chi_1^s/2+\chi_2^s/6$ for a copropagating beam (see Table V, line 2, columns 1 and 2). In particular, for a transition starting from a $J_g=\frac{1}{2}$ ground state ($\chi_2^s=\chi_2^c=0$), a counterpropagating beam will have no effect while some induced effect is expected from a copropagating beam. The fact that a $\chi_1^s$ coefficient appears for linear polarizations arises from the fact that by combining $\mathbf{E}_p$ and $\mathbf{E}_f$ with linear orthogonal polarizations, one obtains a field whose polarization has some circular component (a similar result occurs with $\mathbf{E}_p$ and $\mathbf{E}_b$, but the resulting atomic polarization is vanishingly small because of grating washout). A similar discussion can be made for circularly polarized beams (see Table V, line 6, columns 1 and 2).

Another use of the first column of Table V is that it permits one to determine when the *forward four-wave-mixing* emission may be phase matched. Following [10], one can show that, because of the difference between the nonlinear indices of the pump and the probe, the forward four-wave-mixing emission can be *phase matched* for a value of $\theta$ that satisfies

$$(1+\chi_p/2)\cos\theta=(1+\chi_f/2) , \tag{22}$$

where $\chi_p$ and $\chi_f$ are the effective susceptibilities of the probe and forward pump. For small $\theta$, Eq. (22) yields

$$\theta^2=(\chi_p-\chi_f) . \tag{23}$$

Phase matching is thus possible only on the side of the resonance for which $(\chi_p-\chi_f)$ is positive. The value of $(\chi_p-\chi_f)$ is deduced from the first column of Tables V and III and is reported in Table VI. The polarization of the probe field is essential for this process and completely

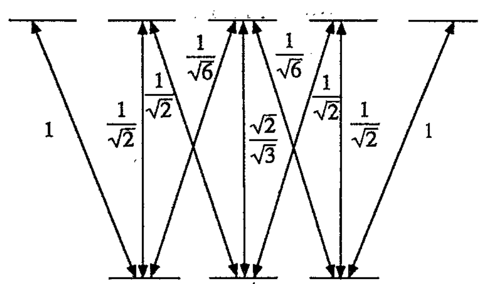


FIG. 2. Scheme of the atomic levels and Clebsch-Gordan coefficients for a $J_g=1\rightarrow J_e=2$ transition.

TABLE IV. Expansion of the forward polarization $P_{fbpc}$ to first order in weak fields $\mathbf{E}_p$ and $\mathbf{E}_c$ for different field polarizations $\mathbf{e}_f$, $\mathbf{e}_b$, $\mathbf{e}_p$, and $\mathbf{e}_c$. Proportionality coefficients versus $a_1$ $a_2$, $a_3$, $b_1$, and $b_2$.

| Coefficient of $P_{fbpc}$ | $\|E_F\|^2 E_p$ | $\|E_b\|^2 E_p$ | $E_f E_b E_c^*$ | $E_f^2 E_p^*$ | $E_f E_b^* E_c$ |
|---|---|---|---|---|---|
| $P_{xxxx}$ | $2a_1+b_1$ | $a_2+a_3+b_2$ | $a_2+a_3+b_2$ | $a_1+\frac{1}{2}b_1$ | $a_2+a_3+b_2$ |
| $P_{xxyy}$ | $a_1$ | $a_2$ | $b_2$ | $\frac{1}{2}b_1$ | $a_3$ |
| $P_{xyxy}$ | $2a_1+b_1$ | $a_2$ | $a_2$ | $a_1+\frac{1}{2}b_1$ | $a_2$ |
| $P_{xyyx}$ | $a_1$ | $a_2+a_3+b_2$ | $a_3$ | $\frac{1}{2}b_1$ | $b_2$ |
| $P_{++++}$ | $2a_1$ | $a_2+a_3$ | $a_2+a_3$ | $a_1$ | $a_2+a_3$ |
| $P_{++--}$ | $a_1+b_1$ | $a_2+b_2$ | 0 | 0 | $a_3+b_2$ |
| $P_{+-+-}$ | $2a_1$ | $a_2+b_2$ | $a_2+b_2$ | $a_1$ | $a_2+b_2$ |
| $P_{+--+}$ | $a_1+b_1$ | $a_2+a_3$ | $a_3+b_2$ | 0 | 0 |

different results are expected for a $y$- and an $x$-polarized probe. For example, for a transition starting from a $J_g=\frac{1}{2}$ ground state ($\chi_2^s=0$), phase matching in a direction $\theta\neq 0$ can only be achieved for a probe beam cross polarized with the pump beam. The side of the resonance for which this effect occurs depends on the sign of $\chi_1^s$ which implies, using Table I, that the emission will be phase matched above resonance for a $J_g=\frac{1}{2}\to J_e=\frac{1}{2}$ transition and below resonance for a $J_g=\frac{1}{2}\to J_e=\frac{3}{2}$ transition (provided that optical pumping is the dominant nonlinear effect).

The third column of Tables IV and V gives the component of the atomic polarization that generates the phase-conjugate beam $E_c$. To maximize *optical phase conjugation,* one needs to have a coefficient whose magnitude is as large as possible. Because most coefficients are linear combination of $\chi_1^c$ and $\chi_2^c$, it is not possible to give general rules valid for any transition and one should calculate the $\chi_k^6$ using Eqs. (15) for each transition under consideration. However, by comparing the first and the third lines of Table V, it is possible to show that the phase-conjugate reflection will be larger by a factor 4 when the counterpropagating beams have the same linear polarization in comparison with the situation where they have orthogonal polarizations, the probe beam having always the same polarization as the forward pump. We note also that, because of angular momentum conservation, phase conjugation is not possible for one configuration of polarization. Note that a complete description of optical pumping effects in optical phase conjugation has been reported by Ducloy and Bloch [11].

Column 4 of Tables IV and V gives the components of the atomic polarization that drives *forward four-wave-mixing* generation. Column 5 of these same tables gives the components of the atomic polarization that generates another four-wave-mixing process sometimes named *distributed feedback.* This contribution appears, for example, in the realization of the *phase-contrast mirror* [12]. For this problem, the interference between the phase-conjugate emission and the distributed feedback emission that propagate in almost the same direction transform the phase variations of a weak incident field into amplitude variations in the reflected field. A good phase-contrast mirror should fulfill several constraints. First, the phase-conjugate emission and the distributed feedback emission should have the same polarization and this polarization has to be orthogonal to the pump polarization to separate easily the reflected beam from the transmitted pump. Second, the phase-conjugate emission and the distributed feedback emission should have similar magnitudes to have the maximum contrast on the reflected beam. The first constraint implies that the only possible situation is described by line 2 of Tables IV and V. In this situation, the coefficients for phase conjugation and distributed feedback generations are, respectively, equal to $(\chi_1^c/2+\chi_2^c/2)$ and $(-\chi_1^c/2+\chi_2^c/2)$. A perfect contrast can only be obtained when $\chi_1^c=0$ or $\chi_2^c=0$. The second possibility ($\chi_2^c=0$) is automatically achieved for a

TABLE V. Expansion of the forward polarization $P_{fbpc}$ to first order in weak fields $\mathbf{E}_p$ and $\mathbf{E}_c$ for different field polarizations $\mathbf{e}_f$, $\mathbf{e}_b$, $\mathbf{e}_p$, and $\mathbf{e}_c$. Proportionality coefficients versus $\chi_1^s$, $\chi_2^s$, $\chi_1^c$, and $\chi_2^c$.

| Coefficient of $P_{fbpc}$ | $\|E_f\|^2 E_p$ | $\|E_b\|^2 E_p$ | $E_f E_b E_c^*$ | $E_f^2 E_p^*$ | $E_f E_b^* E_c$ |
|---|---|---|---|---|---|
| $P_{xxxx}$ | $\frac{4}{3}\chi_2^s$ | $\frac{2}{3}\chi_2^c$ | $\frac{2}{3}\chi_2^c$ | $\frac{2}{3}\chi_2^s$ | $\frac{2}{3}\chi_2^c$ |
| $P_{xxyy}$ | $-\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $-\frac{1}{3}\chi_2^c$ | $\frac{1}{2}\chi_1^c+\frac{1}{2}\chi_2^c$ | $\frac{1}{2}\chi_1^s+\frac{1}{2}\chi_2^s$ | $-\frac{1}{2}\chi_1^c+\frac{1}{2}\chi_2^c$ |
| $P_{xyxy}$ | $\frac{4}{3}\chi_2^s$ | $-\frac{1}{3}\chi_2^c$ | $-\frac{1}{3}\chi_2^c$ | $\frac{2}{3}\chi_2^s$ | $-\frac{1}{3}\chi_2^c$ |
| $P_{xyyx}$ | $-\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $\frac{2}{3}\chi_2^c$ | $-\frac{1}{2}\chi_1^c+\frac{1}{2}\chi_2^c$ | $\frac{1}{2}\chi_1^s+\frac{1}{2}\chi_2^s$ | $\frac{1}{2}\chi_1^c+\frac{1}{2}\chi_2^c$ |
| $P_{++++}$ | $-\chi_1^s+\frac{1}{3}\chi_2^s$ | $-\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | $-\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | $-\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $-\frac{1}{2}\chi_1^c+\frac{1}{2}\chi_2^c$ |
| $P_{++--}$ | $\frac{1}{2}\chi_1^s+\frac{7}{6}\chi_2^s$ | $\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | 0 | 0 | $\chi_2^c$ |
| $P_{+-+-}$ | $-\chi_1^s+\frac{1}{3}\chi_2^s$ | $\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | $\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | $-\frac{1}{2}\chi_1^s+\frac{1}{6}\chi_2^s$ | $\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ |
| $P_{+--+}$ | $\frac{1}{2}\chi_1^s+\frac{7}{6}\chi_2^s$ | $-\frac{1}{2}\chi_1^c+\frac{1}{6}\chi_2^c$ | $\chi_2^c$ | 0 | 0 |

TABLE VI. Difference $(\chi_p - \chi_f)$ between the effective susceptibilities of the probe $\mathbf{E}_p$ and forward pump $\mathbf{E}_f$ for different polarizations $\mathbf{e}_p$ and $\mathbf{e}_f$.

| | $(\chi_p - \chi_f)$ |
|---|---|
| $p=x, f=x$ | $\frac{2}{3}\chi_2^s$ |
| $p=y, f=x$ | $-(\frac{1}{2})\chi_1^s-(\frac{1}{2})\chi_2^s$ |
| $p=+, f=+$ | $-(\frac{1}{2})\chi_1^s+(\frac{1}{6})\chi_2^s$ |

transition starting from a $J_g=\frac{1}{2}$ level. This was actually the experimental conditions of [12].

Finally, we remark that the coefficients of Tables II and III, on one hand, and Tables IV and V, on the other hand, are useful to predict the characteristics of *polarization instability and transverse instability* [6] for a standing wave in a nonlinear medium. For example, it can be seen that when all beams have the same polarization and for $|\delta| \gg ku$, all coefficients are equal, expect for the coefficient of $|E_f|^2 E_p$, which is twice the others. This shows that the equations used to determine the threshold in this configuration will be the same as the one used for a scalar Kerr medium assuming a total grating washout [13]. The predictions (instability threshold versus $\theta$, etc.) can thus be directly deduced from these preceding approaches.

## V. CONCLUSION

We have studied the third-order nonlinear response of an atomic vapor interacting with counterpropagating beams. We have shown that the formal expression of the third-order nonlinear polarization resulting from optical pumping is very different from what is expected from a crude extension of Ref. [1]. This demonstrates that the effect of atomic motion can be important and that its description requires considerable care.

We believe that the expression of the third-order nonlinear polarization given in the present paper is more reliable than the expressions previously used for problems dealing with counterpropagating beams in atomic vapors. However, the present description has still some limitations. First, it often occurs that the effective lifetime of the atomic ground state is associated with transit-time effects through the laser beam. Even though these effects are often described by an empirical relaxation rate $\gamma$, it should be remembered that transit time effects generally do not lead to Lorentzian line shapes. Second, it is well known that even moderate cw laser beams are sufficient to fully saturate an atomic transition. In this case, the description presented in this paper is inappropriate and a nonperturbative approach should be used.

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## APPENDIX

The polarization $\mathbf{P}(\mathbf{r},t)$ is obtained by averaging the atomic polarization of an atom located at $\mathbf{r}$ at time $t$ having velocity $\mathbf{v}$, $\mathbf{P}(\mathbf{r},\mathbf{v},t)$, over the velocity distribution:

$$\mathbf{P}(\mathbf{r},t)=N\int W(\mathbf{v})\mathbf{P}(\mathbf{r},\mathbf{v},t)d^3v \ . \tag{A1}$$

$N$ is the atomic density and $W(\mathbf{v})$ is the Maxwell-Boltzmann distribution.

$\mathbf{P}(\mathbf{r},\mathbf{v},t)$ is equal to the mean value of the electric dipole moment operator $\mathbf{d}$:

$$\mathbf{P}(\mathbf{r},\mathbf{v},t)=\mathrm{Tr}\sigma(\mathbf{r},\mathbf{v},t)\mathbf{d}=\mathrm{Tr}\{\mathbf{d}^-\sigma_{eg}(\mathbf{r},\mathbf{v},t)+\mathrm{H.c.}\} \tag{A2}$$

with

$$\sigma_{eg}(\mathbf{r},\mathbf{v},t)=P_e\sigma(\mathbf{r},\mathbf{v},t)P_g \ , \tag{A3a}$$

$$\mathbf{d}^-=P_g\mathbf{d}P_e \ . \tag{A3b}$$

$\sigma(\mathbf{r},\mathbf{v},t)$ is the density operator for an atom located at $\mathbf{r}$ at time $t$ and having velocity $\mathbf{v}$. $P_g$ and $P_e$ are the projectors onto the ground and excited states, respectively,

$$P_g=\sum_{m_g=-J_g}^{m_g=+J_g}|J_g m_g\rangle\langle J_g m_g| \ , \tag{A4a}$$

$$P_e=\sum_{m_e=-J_e}^{m_e=J_e}|J_e m_e\rangle\langle J_e m_e| \ . \tag{A4b}$$

The atomic density operator $\sigma$ can be written

$$\sigma=\sigma_{gg}+\sigma_{ee}+\sigma_{ge}+\sigma_{eg} \ , \tag{A4c}$$

with

$$\sigma_{ab}=P_a\sigma P_b \quad (a,b=e \text{ or } g) \ .$$

Note that $\sigma_{ab}$ is an operator and not a $c$ number. The two operators $\sigma_{gg}$ and $\sigma_{ee}$ are represented by square matrices. Their diagonal elements give the populations of the various Zeeman sublevels of $g$ and $e$, whereas the off-diagonal elements describe "Zeeman coherences" which exist between them in $e$ or $g$. Finally, $\sigma_{ge}$ and $\sigma_{eg}=\sigma_{ge}^\dagger$ are represented by rectangular matrices consisting of off-diagonal elements between one sublevel of $e$ and one sublevel of $g$, which are called "optical coherences."

The polarization $\mathbf{P}(\mathbf{r},\mathbf{v},t)$ depends on the off-diagonal elements of $\sigma$. We now briefly explain how it is possible to derive equations of motion for $\sigma$. The basic equations of motion, which generalize the Bloch equations [14], can be written in operator form

$$\frac{d}{dt}\sigma_{ab}=-\frac{i}{\hbar}P_a[H_A+V_{AL},\sigma]P_b+\left[\frac{d}{dt}\sigma_{ab}\right]_{\mathrm{sp}} \ , \tag{A5}$$

where $H_A=\hbar\omega_0 P_e$ is the atomic Hamiltonian and $V_{AL}$ describes the atom-field interaction. The last term describes damping due to spontaneous emission. For a moving atom one should use $d/dt=\partial/\partial t+\mathbf{v}\cdot(\partial/\partial\mathbf{r})$. The expression of the interaction Hamiltonian $V_{AL}$ is

$$V_{AL}=-\mathbf{d}^+\cdot\mathbf{E}(\mathbf{r})e^{-i\omega t}-\mathbf{d}^-\cdot\mathbf{E}^*(r)e^{i\omega t} \ , \tag{A6}$$

where $\mathbf{E}(\mathbf{r})$ is the positive-frequency component of the laser field. In the case considered here in which two counterpropagating beams interact with an atomic vapor, $\mathbf{E}(\mathbf{r})$ is given by Eq. (2).

We introduce dimensionless dipole operators $\hat{\mathbf{d}}^{\pm}$ in the following way. Let

$$\mathbf{e}_{\pm}=\mp\frac{1}{\sqrt{2}}(\mathbf{e}_x\pm i\mathbf{e}_y)\ ,\quad \mathbf{e}_0=\mathbf{e}_z \tag{A7}$$

be a spherical basis of polarizations, corresponding respectively to $\sigma_{\pm}$ and $\pi$ polarization. The Wigner-Eckart theorem [15] applied to the vectorial operator $\mathbf{d}^+$ gives

$$\langle J_e m_e|\mathbf{e}_q\cdot\mathbf{d}^+|J_g m_g\rangle=D\langle J_e m_e|J_g 1 m_g q\rangle\ , \tag{A8}$$

where $\langle J_e m_e|J_g 1 m_g q\rangle$ is a Clebsch-Gordan coefficient and $D$ is some reduced matrix element which can always be taken real with an appropriate choice of the relative phases of $e$ and $g$. $D$ can be related to the oscillator strength $f_{ge}$ using the following formula:

$$f_{ge}=\frac{2}{3}\frac{m\omega_0}{\hbar q^2}\frac{2J_e+1}{2J_g+1}D^2\ . \tag{A9}$$

We set $\mathbf{d}^+=D\hat{\mathbf{d}}^+$ so that the matrix elements of $\mathbf{e}_q\cdot\hat{\mathbf{d}}^+$ are just Clebsch-Gordan coefficients. We also introduce the polarization vector $\epsilon_f$ and the intensity $I_f$ of the forward pump field $\mathbf{E}_f$:

$$\mathbf{E}_f=\epsilon_f\sqrt{I_f} \tag{A10a}$$

and similarly for the backward field:

$$\mathbf{E}_b=\epsilon_b\sqrt{I_b}\ . \tag{A10b}$$

The (generally complex) polarization vectors are normalized. The Cartesian components of the field can be expressed as a product of the field amplitude by the Cartesian components of the polarization vector:

$$E_{fx}=\epsilon_{fx}\sqrt{I_f}\ ,\quad E_{fy}=\epsilon_{fy}\sqrt{I_f}\ , \tag{A11a}$$

$$E_{bx}=\epsilon_{bx}\sqrt{I_b}\ ,\quad E_{by}=\epsilon_{by}\sqrt{I_b}\ . \tag{A11b}$$

The last term of Eq. (A5) describes damping due to the spontaneous emission. For the excited-state density operator $\sigma_{ee}$ and for the optical coherences $\sigma_{eg}$ and $\sigma_{ge}$, it keeps the same form as for a two-level atom:

$$\frac{d}{dt}\sigma_{ee}=-\Gamma\sigma_{ee}\ ,\quad \frac{d}{dt}\sigma_{eg}=-\Gamma_{eg}\sigma_{eg}\ , \tag{A12}$$

where $\Gamma$ is the decay rate of the excited level due to spontaneous emission and $\Gamma_{eg}=\Gamma/2$. The feeding of $\sigma_{gg}$ from $\sigma_{ee}$ by spontaneous emission can be written as

$$\left[\frac{d}{dt}\sigma_{gg}\right]_{sp}=T(\sigma_{ee})=\Gamma\sum_{q=0,\pm1}\mathbf{e}_q^*\cdot\hat{\mathbf{d}}^-\sigma_{ee}\mathbf{e}_q\cdot\hat{\mathbf{d}}^+\ . \tag{A13}$$

With those formulas the transfer rate from $e$ to $g$ due to spontaneous emission is equal to the departure rate from $e$. Any atom which leaves the level $e$ returns to level $g$. In the rotating frame $[\tilde{\sigma}_{eg}=\sigma_{eg}\exp(i\omega t)]$, we get the equation of motion:

$$\frac{d}{dt}\sigma_{ee}=-\Gamma\sigma_{ee}+\frac{i}{\hbar}[\mathbf{d}^+\cdot\mathbf{E}\tilde{\sigma}_{ge}-\tilde{\sigma}_{eg}\mathbf{d}^-\cdot\mathbf{E}^*]\ , \tag{A14a}$$

$$\frac{d}{dt}\tilde{\sigma}_{eg}=-(\Gamma_{eg}-i\delta)\tilde{\sigma}_{eg}+\frac{i}{\hbar}[\mathbf{d}^+\cdot\mathbf{E}\sigma_{gg}-\sigma_{ee}\mathbf{d}^+\cdot\mathbf{E}]\ , \tag{A14b}$$

$$\frac{d}{dt}\sigma_{gg}=\left[\frac{d}{dt}\sigma_{gg}\right]_{sp}+\frac{i}{\hbar}[\mathbf{d}^-\cdot\mathbf{E}^*\tilde{\sigma}_{eg}-\tilde{\sigma}_{ge}\mathbf{d}^+\cdot\mathbf{E}]\ . \tag{A14c}$$

Very often other relaxation processes (due, for example, to spin-exchange collisions or to wall collisions) should be included to describe the evolution of the ground state. The typical relaxation time of this process $\gamma^{-1}$ is assumed to be much longer than $\Gamma^{-1}$. In this paper we consider the low saturation limit ($s\ll1$) and we call $(\Gamma')^{-1}$ the characteristic evolution time of $\sigma_{gg}$ caused by the interaction with the laser field. The pumping rate $\Gamma'$ is of the order of $s\Gamma$ and is consequently much smaller than $\Gamma$. Furthermore we assume $\Gamma'$ to be smaller than $\gamma$. In these conditions (which can be summarize by the condition $s\ll\gamma/\Gamma$) we use a perturbative method to third order in field amplitudes to calculate the nonlinear polarization.

Using the notation ${}^{(n)}\sigma$ for the density matrix at the order $n$ of the perturbation expansion, formula (A14b) permits us to express ${}^{(3)}\sigma_{eg}$ versus ${}^{(2)}\sigma_{gg}$ and ${}^{(2)}\sigma_{ee}$. When $ku\gg\Gamma\gg\gamma$, the main contribution to ${}^{(3)}\sigma_{eg}$ comes from the two spatially independent components of ${}^{(2)}\sigma_{gg}$: the first one ${}_f\sigma_g$ results from optical pumping induced by the forward beam and the second one ${}_b\sigma_g$ from optical pumping induced by the backward beam. Since these beams are monochromatic, the optical pumping is velocity selective [16].

Starting with ${}^{(0)}\sigma_{gg}=P_g/(2J_g+1)$ and using Eqs. (A14a) and (A14b), one finds the density matrix of the upper level to second order:

$${}_f\sigma_e(v_z)=\frac{1}{2J_g+1}\frac{1}{\hbar^2\left[\delta_f^2+\frac{\Gamma^2}{4}\right]}\mathbf{d}^+\cdot\mathbf{E}_f P_g\mathbf{d}^-\cdot\mathbf{E}_f^* \tag{A15}$$

with $\delta_f=\delta-kv_z$. A similar expression is obtained for ${}_b\sigma_e(v_z)$ by exchanging the subscripts $f$ and $b$ ($\delta_b$ being defined as $\delta_b=\delta+kv_z$).

The steady-state solution for ${}_f\sigma_g$ is derived from Eqs. (A13), (A14c), and (A15):

$$0=-\frac{{}_f\Gamma'(v)}{2J_g+1}{}_f\Lambda_g+\frac{{}_f\Gamma'(v)}{2J_g+1}\sum_q\mathbf{e}_q^*\cdot\hat{\mathbf{d}}^-{}_f\Lambda_e\mathbf{e}_q\cdot\mathbf{d}^+ + \left[\frac{d}{dt}{}_f\sigma_g\right]_{\mathrm{rel}} \tag{A16}$$

with

$$ {}_f\Gamma'(v)=\frac{\Gamma D^2 I_f}{\hbar^2\left[\delta_f^2+\frac{\Gamma^2}{4}\right]} , \quad (A17a) $$

$$ {}_f\Lambda_g=\hat{\mathbf{d}}^-\cdot\epsilon_f^* P_e \hat{\mathbf{d}}^+\cdot\epsilon_f , \quad (A17b) $$

$$ {}_f\Lambda_e=\hat{\mathbf{d}}^+\cdot\epsilon_f P_g \hat{\mathbf{d}}^-\cdot\epsilon_f^* . \quad (A17c) $$

The first term of (A16) describes absorption. The second one corresponds to repopulation of the ground state from the excited state by spontaneous emission. The third term describes the relaxation of the ground state. Equation (A16) is solved by projecting ${}_f\sigma_g$ and ${}_f\Lambda_a$ $(a=g,e)$ on an irreducible tensorial set basis [17], the components of ${}_f\Lambda_g$ and ${}_f\Lambda_e$ being [18]

$$ {}_f\Lambda_{g_q}^{(k)}=(-1)^k B_k(J_g,J_e)\phi_q^{(k)}(\epsilon_f) , \quad (A18a) $$

$$ {}_f\Lambda_{e_q}^{(k)}=B_k(J_e,J_g)\phi_q^{(k)}(\epsilon_f) , \quad (A18b) $$

where $B_k(J_g,J_e)$ is given by Eq. (16a) and $\phi_q^{(k)}(\epsilon)$ is equal to [18]

$$ \phi_q^{(k)}(\epsilon)=\sum_{p=0,\pm1}(-1)^{p+1}\alpha_{p'}^*\alpha_{-p}\langle 11pp'|kq\rangle \quad (A19) $$

with $\alpha_{-p}=(-1)^p\epsilon\cdot\mathbf{e}_p$.

One then obtains (for $k\geq 1$)

$$ \gamma_k\,{}_f\sigma_{g_q}^{(k)}(v)=\frac{{}_f\Gamma'_g(v)}{(2J_g+1)}\bar{B}_k(J_g,J_e)\phi_q^{(k)}(\epsilon_f) , \quad (A20) $$

where $\gamma_k$ is the relaxation rate of the multipolar operator of rank [for an isotropic relaxation, the rates depend only of $k$ and $\bar{B}_k$ is given by Eq. (A16b)]. To write Eq. (A20) we assume that the velocity-changing collisions fully destroy the anisotropic observables. If a partial conservation of the anisotropic observables occurs during the velocity-changing collisions it is necessary to add a term proportional to the rate of transfer of this observable between different velocity groups [19].

The $\phi_q^{(k)}$ coefficients can be expressed as a function of the Cartesian components of $\epsilon_f$ [18]. Because the beams propagate along the $z$ axis only $\phi_0^{(1)}$, $\phi_{\pm2}^{(2)}$, and $\phi_0^{(2)}$ are different from zero:

$$ \phi_0^{(1)}=\sqrt{2}\,\mathrm{Im}(\epsilon_{fx}^*\epsilon_{fy}) , \quad (A21a) $$

$$ \phi_{\pm2}^{(2)}=\tfrac{1}{2}(|\epsilon_{fy}|^2-|\epsilon_{fx}|^2)\pm\frac{i}{2}(\epsilon_{fx}^*\epsilon_{fy}+\epsilon_{fx}\epsilon_{fy}^*) , \quad (A21b) $$

$$ \phi_0^{(2)}=\frac{1}{\sqrt{6}} . \quad (A21c) $$

From (A20) and (A21), we obtain

$$ {}_f\sigma_{g0}^{(1)}=\frac{\Gamma}{\gamma_1}\frac{D^2}{\hbar^2\left[\delta_f^2+\frac{\Gamma^2}{4}\right]}\frac{1}{2J_g+1}\bar{B}_1\sqrt{2}\,\mathrm{Im}E_{fx}^*E_{fy} , \quad (A22a) $$

$$ {}_f\sigma_{g\pm2}^{(2)}=\frac{\Gamma}{\gamma_2}\frac{D^2}{\hbar^2\left[\delta_f^2+\frac{\Gamma^2}{4}\right]}\frac{1}{2J_g+1}\frac{\bar{B}_2}{2}\times[(|E_{fy}|^2-|E_{fx}|^2\pm2i\,\mathrm{Re}E_{fx}^*E_{fy})] , \quad (A22b) $$

$$ {}_f\sigma_{g0}^{(2)}=\frac{\Gamma}{\gamma_2}\frac{D^2}{\hbar^2\left[\delta_f^2+\frac{\Gamma^2}{4}\right]}\frac{1}{2J_g+1}\frac{\bar{B}_2}{\sqrt{6}}I_f . \quad (A22c) $$

The components ${}_b\sigma_{gq}^{(k)}$ of ${}_b\sigma_g$ are given by exchanging the subscripts $f$ and $b$ everywhere in Eqs. (A22).

From the knowledge of ${}_f\sigma_g$ and ${}_f\sigma_g$, one can deduce the optical coherence ${}^{(3)}\sigma_{eg}$ using Eq. (A14b) and $\mathbf{P}(\mathbf{r},\mathbf{v},t)$ using Eq. (A2)

$$ \mathbf{P}(\mathbf{r},\mathbf{v},t)=-e^{-i\omega t}\mathrm{Tr}\left\{\left[\mathbf{d}^-\left[\frac{\mathbf{d}^+\cdot\mathbf{E}_f}{\hbar}\right]\frac{e^{ikz}}{\delta_f+i\frac{\Gamma}{2}}+\mathbf{d}^-\left[\frac{\mathbf{d}^+\cdot\mathbf{E}_b}{\hbar}\right]\frac{e^{-ikz}}{\delta_b+i\frac{\Gamma}{2}}\right]\times[{}_f\sigma_g+{}_b\sigma_g]\right\}+\mathrm{H.c.} \quad (A23) $$

Finally, the Cartesian component $P_{fi}$ is determined from Eqs. (3), (A1), and (A23)

$$ P_{fi}=-\sum_j\left[\frac{ND^2}{\hbar}\int\frac{W(v)dv}{\delta_f+i\frac{\Gamma}{2}}\mathrm{Tr}(\hat{d}_i^-\hat{d}_j^+)\times[{}_f\sigma_g(v)+{}_b\sigma_g(v)]\right]E_{fj} . \quad (A24) $$

To calculate the mean value of $\hat{d}_i^-\hat{d}_j^+$, it is convenient to expand these operators on the irreducible set basis $T_q^k$:

$$ \hat{d}_x^-\hat{d}_x^+=\frac{1}{\sqrt{6}}[B_2T_0^{(2)}+\sqrt{2}B_0T^{(0)}]-\tfrac{1}{2}B_2[T_2^{(2)}+T_{-2}^2] , \quad (A25a) $$

$$ \hat{d}_y^-\hat{d}_y^+=\frac{1}{\sqrt{6}}[B_2T_0^2+\sqrt{2}B_0T^{(0)}]+\tfrac{1}{2}B_2[T_2^2+T_{-2}^2] , \quad (A25b) $$

$$ \hat{d}_x^-\hat{d}_y^+=i\left[-\frac{B_1}{\sqrt{2}}T_0^1+\frac{B_2}{2}(T_2^2-T_{-2}^2)\right] , \quad (A25c) $$

$$ \hat{d}_y^-\hat{d}_x^+=(\hat{d}_x^-\hat{d}_y^+)^+ , \quad (A25d) $$

where $B_k=B_k(J_g,J_e)$ is given by Eq. (16a). Using

$$ \mathrm{Tr}\{T_q^k\,{}_i\sigma_g\}=(-1)^q\,{}_i\sigma_{g-q}^{(k)} \quad (i=f,b) , \quad (A26) $$

and Eqs. (A22) and (A24), one finds the values given by Eqs. (20) and (21) for $\chi_{ij}^{(0)}$ and $\chi_{ij}^{(2k)}$.

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