Effect of spontaneous emission and recombination on the four-wave–mixing profiles involving autoionizing resonances

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A general expression for the four-wave–mixing profiles in situations involving autoionizing resonances is derived by taking fully into account the spontaneous-emission characteristics of the autoionizing states. The signals are valid for arbitrary values of Fano asymmetry parameters, field strengths, and spontaneous-emission rates. The dramatic increase in the four-wave–mixing signal for field strengths corresponding to the confluence is demonstrated. The spontaneous emission is shown to affect the line shapes not only in weak fields but also in strong fields. The effects of spontaneous emission are found to be most important for field strengths corresponding to confluence which is similar to the problem of laser-induced autoionization.

I. INTRODUCTION

Four-wave mixing involving an autoionizing resonance[1] has been suggested as an important method of producing vacuum ultraviolet (vuv) radiation.[2,3] Armstrong and Wynne first experimentally studied four-wave mixing in such a situation in great detail. A correct theoretical interpretation of their experimental results was given by Armstrong and Beers.[3] Recently Crance and Armstrong and Alber and Zoller have examined the four-wave mixing when the autoionizing state is resonantly pumped from the intermediate state.[5,6] Crance and Armstrong demonstrated that, under certain conditions on the laser field strengths and detuning, a very large four-wave–mixing signal is possible. However, Crance and Armstrong treated the spontaneous emission in a phenomenological manner. It is known[7] from the work of Agarwal *et al.* that the spontaneous emission has a very significant effect on photoemission from autoionizing states in strong fields.[8–10] Similarly, it is also known that the recombination effects[11,12] play an important role in photoemission. Therefore it is desirable to have a general theory of four-wave mixing involving autoionizing resonances in which spontaneous emission has been consistently accounted for. This is all the more important if one wants to achieve laser action in vuv using such resonances.

In Sec. II we describe our model and derive the dynamical equations for the density-matrix elements by taking into account completely the spontaneous emission and recombination effects. In Sec. III the general solution of the dynamical equations is given for an arbitrary continuum. Simpler expressions for the four-wave–mixing signal are presented in Sec. IV by taking the unperturbed continuum to be flat. The results of numerical computations are also given in Sec. IV. The analysis is carried out for arbitrary values of the spontaneous-emission rates, Fano asymmetry parameters, and the laser field strengths. A brief comparison with the results of Crance and Armstrong is also made.[13] The main body of the paper deals with dynamical equations for the matter only since Shen[14] has shown that the steady-state generation of the fourth wave can be calculated easily in terms of the steady-state polarization of the atomic system.

II. MODEL AND THE BASIC FORMULATION

In order to describe the salient features of the four-wave mixing when an autoionizing resonance is involved, we consider the simplified model schematically shown in Fig. 1. Here the initial bound state $|g\rangle$ and the intermediate bound state $|i\rangle$ are weakly coupled by a two-photon transition with the energy separation $\epsilon_{ig}\sim 2\omega_2$. The intermediate state $|i\rangle$ is coupled to the autoionizing state $|a\rangle$ and the unperturbed continuum $|\epsilon)$ by a laser at the frequency ω_1. We allow for the possibility that the laser at ω_1 has an arbitrary intensity. The autoionizing state decays to $|i\rangle$ and $|g\rangle$ by spontaneous emission of photons. We denote the corresponding transition rates by γ_1 and γ_2, respectively. Similarly, the unperturbed continuum can decay to $|i\rangle$ and $|g\rangle$, i.e., the recombination can take place. These recombination rates can be related to the spontaneous-emission rates γ's and Fano's asymmetry parameters q's for the two transitions. We find it convenient to work with the continuum of states $|\epsilon\rangle$ obtained by diagonalizing the configuration interaction be-

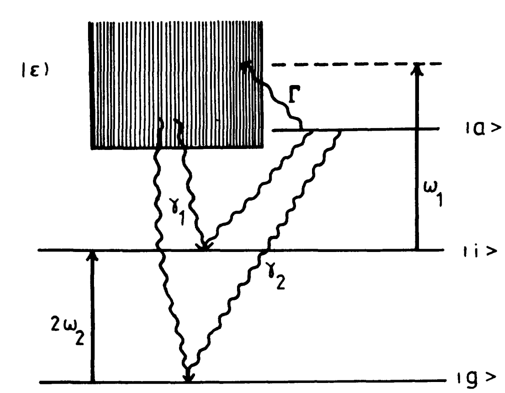

FIG. 1. Schematic diagram of the various energy levels and the rates involved in the transition.

tween $|a\rangle$ and $|\epsilon\rangle$:

$$|\epsilon\rangle = b(\epsilon,a)|a\rangle + \int b(\epsilon,\epsilon')|\epsilon'\rangle d\epsilon' , \tag{2.1}$$

where, as shown by Fano,[1]

$$b(\epsilon,a) = \sin\Delta/\pi V_\epsilon , \quad \tan^{-1}\Delta \cong -\pi |V_\epsilon|^2/(\epsilon-\epsilon_a) ,$$
$$b(\epsilon,\epsilon') = \frac{V_{\epsilon'}}{\pi V_\epsilon}\frac{\sin\Delta}{\epsilon-\epsilon'} - \cos\Delta\,\delta(\epsilon-\epsilon') . \tag{2.2}$$

The parameter V_ϵ is related to the autoionization rate $\Gamma = 2\pi |V_\epsilon|^2$. In writing (2.2) we have ignored the small frequency shift terms. The spontaneous emission and the recombination can be discussed in the framework of master equations.[7] One can show that the density matrix ρ of the atomic system satisfies the following master equation:

$$\frac{\partial\rho}{\partial t} = -i[H,\rho] - \frac{\gamma_1}{2}(A_1^\dagger A_1\rho - 2A_1\rho A_1^\dagger + \rho A_1^\dagger A_1)$$
$$- \frac{\gamma_2}{2}(A_2^\dagger A_2\rho - 2A_2\rho A_2^\dagger + \rho A_2^\dagger A_2) , \tag{2.3}$$

where

$$A_1 = \int d\epsilon\, |i\rangle\langle\epsilon| B_{\epsilon a} , \quad B_{\epsilon a} = \langle a|\epsilon\rangle \left[1 + 2\frac{(\epsilon-\epsilon_a)}{\Gamma q_1}\right] ,$$
$$A_2 = \int d\epsilon\, |g\rangle\langle\epsilon| C_{\epsilon a} , \quad C_{\epsilon a} = \langle a|\epsilon\rangle \left[1 + 2\frac{(\epsilon-\epsilon_a)}{\Gamma q_2}\right] , \tag{2.4}$$

and H represents all the coherent interactions including those corresponding to the two-photon transition $|g\rangle \leftrightarrow |i\rangle$. Thus, H is given by

$$H \equiv \epsilon_i |i\rangle\langle i| + \epsilon_g |g\rangle\langle g| + \int d\epsilon\, |\epsilon\rangle\langle\epsilon|\epsilon$$
$$+ \int d\epsilon (v_{\epsilon i}|\epsilon\rangle\langle i| e^{-i\omega_1 t} + \text{c.c.})$$
$$+ (\mathscr{K}|i\rangle\langle g| e^{-2i\omega_2 t} + \text{c.c.}) , \tag{2.5}$$

where $\mathscr{K}$ is the two-photon matrix element. The parameters γ_1 and γ_2 correspond to the spontaneous emission in the two decay channels. Fano parameters q_1 and q_2 are defined by

$$q_1 \cong \frac{(a|V|i)}{\pi V_\epsilon (\epsilon|V|i)} , \quad q_2 \cong \frac{(a|V|g)}{\pi V_\epsilon (\epsilon|V|g)} .$$

On making a unitary transformation with

$$h = \omega_1 |i\rangle\langle i| + (2\omega_2+\omega_1)|g\rangle\langle g| , \tag{2.6}$$

we can reduce (2.3) to

$$\frac{\partial\tilde\rho}{\partial t} = -i[\tilde H,\tilde\rho] - \sum_i \frac{\gamma_i}{2}(A_i^\dagger A_i\tilde\rho - 2A_i\tilde\rho A_i^\dagger + \tilde\rho A_i^\dagger A_i) , \tag{2.7}$$

where

$$\tilde\rho = e^{-iht}\rho e^{iht} , \tag{2.8}$$
$$\tilde H = (\epsilon_i+\omega_1)|i\rangle\langle i| + (\epsilon_g + 2\omega_2 + \omega_1)|g\rangle\langle g|$$
$$+ \int d\epsilon\, |\epsilon\rangle\langle\epsilon|\epsilon + \left[\int d\epsilon\, v_{\epsilon i}|\epsilon\rangle\langle i| + \text{c.c.}\right]$$
$$+ (\mathscr{K}|i\rangle\langle g| + \text{c.c.}) . \tag{2.9}$$

The four-wave—mixing signal, i.e., the signal produced at $2\omega_2+\omega_1$ will be determined from the polarization produced at $(2\omega_2+\omega_1)$. The induced polarization at $2\omega_2+\omega_1$ can be obtained from the density-matrix element $\rho_{\epsilon g}$ as the following argument shows. Ignoring the vectorial properties, we can write the dipole matrix element as

$$d_{g\epsilon} = d_{ga} C_{\epsilon a} \tag{2.10}$$

and hence the term relevant for four-wave mixing in the induced polarization is

$$P = \langle d\rangle = \int d\epsilon\, \mathrm{Tr}(\rho d_{g\epsilon} |g\rangle\langle\epsilon| + \text{c.c.})$$
$$= \int d\epsilon\, d_{g\epsilon}\rho_{\epsilon g} + \text{c.c} \tag{2.11}$$
$$= d_{ga}\int d\epsilon\, C_{\epsilon a}\tilde\rho_{\epsilon g} e^{-i(2\omega_2+\omega_1)t} + \text{c.c.} , \tag{2.12}$$

where we have also put $\epsilon_g = 0$. We thus need to calculate

$$P = d_{ga}\int d\epsilon\, C_{\epsilon a}\tilde\rho_{\epsilon g} , \tag{2.13}$$

where $\tilde\rho_{\epsilon g}$ in the steady state is obtained from the solution of Eq. (2.7) which can be solved exactly. However, in what follows we treat the important case when $\mathscr{K}$ is small so that a first-order perturbation theory with respect to $\mathscr{K}$ is sufficient. For this purpose we rewrite (2.7) as (dropping the tildes)

$$\frac{\partial\rho}{\partial t} = L\rho - i[(\mathscr{K}|i\rangle\langle g| + \mathscr{K}^*|g\rangle\langle i|),\rho] \tag{2.14}$$

and hence

$$\frac{\partial\rho^{(0)}}{\partial t} = L\rho^{(0)} , \tag{2.15}$$
$$\frac{\partial\rho^{(1)}}{\partial t} = L\rho^{(1)} - i[(\mathscr{K}|i\rangle\langle g| + \mathscr{K}^*|g\rangle\langle i|),\rho^{(0)}] . \tag{2.16}$$

The solution of (2.15) is trivial as, initially, the atom is in the state $|g\rangle$,

$$\rho^{(0)}(t) = |g\rangle\langle g| . \tag{2.17}$$

In view of (2.17), (2.16) reduces to

$$\frac{\partial\rho^{(1)}}{\partial t} = L\rho^{(1)} - i\mathscr{K}|i\rangle\langle g| + i\mathscr{K}^*|g\rangle\langle i| . \tag{2.18}$$

The solution of (2.18) is discussed in Sec. III. For the sake of completeness we now record various elements of $L\rho$:

$$\dot\rho^{(1)}_{\epsilon_1\epsilon_2} = -i(\epsilon_1-\epsilon_2)\rho^{(1)}_{\epsilon_1\epsilon_2} - iv_{\epsilon_1 i}\rho^{(1)}_{i\epsilon_2} + iv^*_{\epsilon_2 i}\rho_{\epsilon_1 i} - \frac{\gamma_1}{2}\int d\epsilon\, B^*_{\epsilon_1 a}B_{\epsilon a}\rho^{(1)}_{\epsilon\epsilon_2} - \frac{\gamma_2}{2}\int d\epsilon\, C^*_{\epsilon_1 a}C_{\epsilon a}\rho^{(1)}_{\epsilon\epsilon_2}$$
$$- \frac{\gamma_1}{2}\int d\epsilon\, B_{\epsilon_2 a}B^*_{\epsilon a}\rho^{(1)}_{\epsilon_1\epsilon} - \frac{\gamma_2}{2}\int d\epsilon\, C_{\epsilon_2 a}C^*_{\epsilon a}\rho^{(1)}_{\epsilon_1\epsilon} , \tag{2.19}$$

$$\dot{\rho}^{(1)}_{\epsilon_1 i}=-i(\epsilon_1-\omega_1-\epsilon_i)\rho^{(1)}_{\epsilon_1 i}-i\left[v_{\epsilon_1 i}\rho^{(1)}_{ii}-\int d\epsilon\,\rho^{(1)}_{\epsilon_1\epsilon}v_{\epsilon i}\right]-\frac{\gamma_1}{2}\int d\epsilon\,B^*_{\epsilon_1 a}B_{\epsilon a}\rho^{(1)}_{\epsilon i}-\frac{\gamma_2}{2}\int d\epsilon\,C^*_{\epsilon_1 a}C_{\epsilon a}\rho^{(1)}_{\epsilon i}\ , \tag{2.20}$$

$$\dot{\rho}^{(1)}_{\epsilon_1 g}=-i(\epsilon_1-\omega_1-2\omega_2)\rho^{(1)}_{\epsilon_1 g}-iv_{\epsilon_1 i}\rho^{(1)}_{ig}-\frac{\gamma_1}{2}\int d\epsilon\,B^*_{\epsilon_1 a}B_{\epsilon a}\rho^{(1)}_{\epsilon g}-\frac{\gamma_2}{2}\int d\epsilon\,C^*_{\epsilon_1 a}C_{\epsilon a}\rho^{(1)}_{\epsilon g}\ , \tag{2.21}$$

$$\dot{\rho}^{(1)}_{ig}=-i(\epsilon_i-2\omega_2)\rho^{(1)}_{ig}-i\int v^*_{\epsilon i}\rho^{(1)}_{\epsilon g}d\epsilon-i\mathscr{K}\ , \tag{2.22}$$

$$\dot{\rho}^{(1)}_{ii}=-i\int v^*_{\epsilon i}\rho^{(1)}_{\epsilon i}d\epsilon+\frac{\gamma_1}{2}\int d\epsilon_1\int d\epsilon\,B^*_{\epsilon_1 a}B_{\epsilon a}\rho^{(1)}_{\epsilon\epsilon_1}+\text{c.c.}\ , \tag{2.23}$$

and

$$\dot{\rho}^{(1)}_{gg}=\frac{\gamma_2}{2}\int d\epsilon_1\int d\epsilon\,C^*_{\epsilon_1 a}C_{\epsilon a}\rho^{(1)}_{\epsilon\epsilon_1}+\text{c.c.} \tag{2.24}$$

III. EXACT SOLUTION OF THE DENSITY-MATRIX EQUATION (2.18)

The density-matrix equation (2.18) has a rather complicated structure. In order to solve (2.18) we make use of the technique that was used earlier[7,12] in connection with the simpler problem of laser-induced autoionization, in which one solves for a set of auxiliary density matrices and then the solution of the full equation is constructed in terms of such density matrices. For this purpose we rewrite (2.18) as

$$\dot{\rho}^{(1)}=\mathscr{L}\rho^{(1)}+I_i(t)\,|\,i\,\rangle\langle\,i\,|+I_g(t)\,|\,g\,\rangle\langle\,g\,|-i\mathscr{K}\,|\,i\,\rangle\langle\,g\,|+i\mathscr{K}^*\,|\,g\,\rangle\langle\,i\,|\ , \tag{3.1}$$

where

$$I_i(t)=\mathrm{Tr}\left[\rho^{(1)}(t)\left[\frac{\gamma_1}{2}\int d\epsilon_1\int d\epsilon\,B^*_{\epsilon_1 a}B_{\epsilon a}\,|\,\epsilon_1\rangle\langle\,\epsilon\,|+\text{H.c.}\right]\right]\ , \tag{3.2}$$

$$I_g(t)=\mathrm{Tr}\left[\rho^{(1)}(t)\left[\frac{\gamma_2}{2}\int d\epsilon_1\int d\epsilon\,C^*_{\epsilon_1 a}C_{\epsilon a}\,|\,\epsilon_1\rangle\langle\,\epsilon\,|+\text{H.c.}\right]\right]\ . \tag{3.3}$$

In Eq. (3.1), $\mathscr{L}$ is a simplified Liouville operator and is defined below. Let us now introduce a density matrix σ with elements

$$\begin{aligned}&\sigma_{\epsilon_1\epsilon_2}(t)=\psi_{\epsilon_1}(t)\psi^*_{\epsilon_2}(t)\ ,\quad \sigma_{\epsilon_1 i}(t)=\psi_{\epsilon_1}(t)\psi^*_i(t)\ ,\\ &\sigma_{\epsilon_1 g}(t)=\psi_{\epsilon_1}(t)\psi^*_g(t)\ ,\\ &\sigma_{ii}(t)=|\,\psi_i\,|^2,\quad \sigma_{gg}(t)=|\,\psi_g\,|^2\ ,\\ &\sigma_{ig}(t)=\psi_i(t)\psi^*_g(t)\ ,\end{aligned} \tag{3.4}$$

whose equations of motion are

$$\dot{\sigma}=\mathscr{L}\sigma\ , \tag{3.5}$$

where $\mathscr{L}$ is now defined in terms of the equations of motion for ψ's:

$$\dot{\psi}_{\epsilon_1}=-i\Delta_{\epsilon_1 i}\psi_{\epsilon_1}-iv_{\epsilon_1 i}\psi_i-\frac{\gamma_1}{2}\int d\epsilon\,B^*_{\epsilon_1 a}B_{\epsilon a}\psi_\epsilon-\frac{\gamma_2}{2}\int d\epsilon\,C^*_{\epsilon_1 a}C_{\epsilon a}\psi_\epsilon\ , \tag{3.6}$$

$$\dot{\psi}_i=-i\int v^*_{\epsilon i}\psi_\epsilon d\epsilon\ , \tag{3.7}$$

$$\dot{\psi}_g=-iv\psi_g,\quad v=2\omega_2-\epsilon_i,\quad \Delta_{\epsilon_1 i}=\epsilon_1-\omega_1-\epsilon_i\ . \tag{3.8}$$

We now show how the solution of (3.1) can be obtained in terms of σ_i. One obviously has from (3.1)

$$\rho^{(1)}(t)=\int_0^t d\tau[I_i(\tau)e^{\mathscr{L}(t-\tau)}\,|\,i\,\rangle\langle\,i\,|+I_g(\tau)e^{\mathscr{L}(t-\tau)}\,|\,g\,\rangle\langle\,g\,|-i\mathscr{K}e^{\mathscr{L}(t-\tau)}\,|\,i\,\rangle\langle\,g\,|+i\mathscr{K}^*e^{\mathscr{L}(t-\tau)}\,|\,g\,\rangle\langle\,i\,|\,] \tag{3.9}$$

and from (3.5)

$$\sigma(t)=e^{\mathscr{L}t}\sigma(0)\ . \tag{3.10}$$

We solve the set [(3.6)—(3.8)] subject to the arbitrary initial condition on ψ_i and ψ_g, i.e., we assume

$$\sigma(0)=|\,\psi_i\,|^2\,|\,i\,\rangle\langle\,i\,|+|\,\psi_g\,|^2\,|\,g\,\rangle\langle\,g\,|+\psi_i\psi^*_g\,|\,i\,\rangle\langle\,g\,|+\psi_g\psi^*_i\,|\,g\,\rangle\langle\,i\,|$$

and then one has

$$\sigma(t)=|\,\psi_i\,|^2e^{\mathscr{L}t}\,|\,i\,\rangle\langle\,i\,|+|\,\psi_g\,|^2e^{\mathscr{L}t}\,|\,g\,\rangle\langle\,g\,|+\psi_i\psi^*_g e^{\mathscr{L}t}\,|\,i\,\rangle\langle\,g\,|+\psi^*_i\psi_g e^{\mathscr{L}t}\,|\,g\,\rangle\langle\,i\,|\ , \tag{3.11}$$

which, on using the definition (3.4), can be written as

$$\sigma(t)=|\psi_i(t)|^2|i\rangle\langle i|+|\psi_g(t)|^2|g\rangle\langle g|+\psi_i^*(t)\psi_g(t)|g\rangle\langle i|+\psi_i(t)\psi_g^*(t)|i\rangle\langle g|$$
$$+\int d\epsilon_1\int d\epsilon_2\psi_{\epsilon_1}^*(t)\psi_{\epsilon_2}(t)|\epsilon_2\rangle\langle\epsilon_1|+\int d\epsilon_1\psi_{\epsilon_1}(t)\psi_g^*(t)|\epsilon_1\rangle\langle g|+\int d\epsilon_1\psi_{\epsilon_1}^*(t)\psi_g(t)|g\rangle\langle\epsilon_1|$$
$$+\int d\epsilon_1\psi_{\epsilon_1}(t)\psi_i^*(t)|\epsilon_1\rangle\langle i|+\int d\epsilon_1\psi_{\epsilon_1}^*(t)\psi_i(t)|i\rangle\langle\epsilon_1| \ . \qquad (3.12)$$

We now write the solution of (3.6)—(3.8) in the form

$$\psi_g(t)=e^{-i\nu t}\psi_g(0),\quad \psi_i(t)=S_i(t)\psi_i(0),\quad \psi_\epsilon(t)=S_\epsilon(t)\psi_i(0) \qquad (3.13)$$

and substitute in (3.12) and then compare the coefficients of $\psi_i(0)$ and $\psi_g(0)$ since $\psi_i(0)$ and $\psi_g(0)$ are taken to be completely arbitrary. This procedure leads to the following operator relations:

$$e^{\mathcal{L}t}|g\rangle\langle g|=|g\rangle\langle g| \ , \qquad (3.14)$$

$$e^{\mathcal{L}t}|i\rangle\langle i|=|S_i|^2|i\rangle\langle i|+\int d\epsilon_1\int d\epsilon_2 S_{\epsilon_1}^*(t)S_{\epsilon_2}(t)|\epsilon_2\rangle\langle\epsilon_1|+\int d\epsilon_1 S_{\epsilon_1}(t)S_i^*(t)|\epsilon_1\rangle\langle i|$$
$$+\int d\epsilon_1 S_{\epsilon_1}^*(t)S_i(t)|i\rangle\langle\epsilon_1| \ , \qquad (3.15)$$

$$e^{\mathcal{L}t}|i\rangle\langle g|=S_i(t)e^{+i\nu t}|i\rangle\langle g|+\int d\epsilon_1 S_{\epsilon_1}(t)e^{+i\nu t}|\epsilon_1\rangle\langle g| \ , \qquad (3.16)$$

$$e^{\mathcal{L}t}|g\rangle\langle i|=S_i^*(t)e^{-i\nu t}|g\rangle\langle i|+\int d\epsilon_1 S_{\epsilon_1}^*(t)e^{-i\nu t}|g\rangle\langle\epsilon_1| \ . \qquad (3.17)$$

We now return to Eq. (3.9) and evaluate $I_i(t)$ and $I_g(t)$. From (3.16) and (3.17) we have the important relation

$$\langle\epsilon_1|(e^{\mathcal{L}t}|i\rangle\langle g|)|\epsilon_2\rangle=0 \ ,$$
$$\langle\epsilon_1|(e^{\mathcal{L}t}|g\rangle\langle i|)|\epsilon_2\rangle=0 \ . \qquad (3.18)$$

On using (3.2), (3.3), and (3.18) in (3.9) we find the result

$$I_i(t)=I_g(t)=0 \ . \qquad (3.19)$$

On substituting (3.19), (3.16), and (3.17) we obtain for the Laplace transform of $\rho^{(1)}$

$$\hat{\rho}^{(1)}(z)=-i\mathcal{K}\hat{S}_i(z-i\nu)z^{-1}|i\rangle\langle g|$$
$$-i\mathcal{K}\int d\epsilon_1\hat{S}_{\epsilon_1}(z-i\nu)z^{-1}|\epsilon_1\rangle\langle g|+\text{c.c.} \qquad (3.20)$$

The steady-state value of $\rho_{\epsilon g}^{(1)}$ is given by

$$\tilde{\rho}_{\epsilon g}^{(1)}(t\to\infty)=\lim_{z\to 0}z\hat{\rho}_{\epsilon g}^{(1)}(z)=-i\mathcal{K}S_\epsilon(-i\nu) \qquad (3.21)$$

and hence the quantity P [defined by (2.13)] which is relevant for four-wave signal becomes

$$P=-i\mathcal{K}\int d\epsilon\, C_{\epsilon a}\hat{S}_\epsilon(-i\nu)d_{ga} \ . \qquad (3.22)$$

It should be remembered that $S_\epsilon(t)$ is the solution of (3.6) and (3.7) is subject to the initial condition $\psi_i(0)=1$, $\psi_\epsilon(0)=0$. We derive the complete solution of (3.6) and (3.7) in the Appendix. Using the solution given in the Appendix we can write (3.22) as

$$P=-i\mathcal{K}\left[\frac{2}{\gamma_2}\right]^{1/2}\hat{\psi}_3(-i\nu)d_{ga}$$
$$=-d_{ga}\mathcal{K}\left[\frac{2}{\gamma_2}\right]^{1/2}\sum_j[(\underline{1}+\underline{m})^{-1}]_{3j}m_{j1}\Big|_{z=-i\nu}$$
$$=\mathcal{K}\left[\frac{2}{\gamma_2}\right]^{1/2}d_{ga}[(\underline{1}+\underline{m})^{-1}]_{31}\Big|_{z=-i\nu} \ , \qquad (3.23)$$

where the matrix $\underline{m}$ is defined by (A5).

IV. DETAILED FEATURES OF THE FOUR-WAVE–MIXING SIGNAL

In this section we obtain the general form of the four-wave–mixing signal, which is valid for arbitrary values of the field intensity associated with the laser at ω_1, and for arbitrary values of the spontaneous-emission rates. On using (A6) and (A10) and on introducing the parameter x defined by

$$x=\frac{2}{\Gamma}(\epsilon_a-\omega_1-2\omega_2) \ , \qquad (4.1)$$

Eq. (3.23) can be written as

$$P=2i\mathcal{K}d_{ga}S(x) \ , \qquad (4.2)$$

$$S(x)\equiv\sqrt{\Omega}q_1\left[1-\frac{i}{q_1}-\frac{i}{q_2}+\frac{ix}{q_1q_2}\right]\Big/D \ . \qquad (4.3)$$

Here the polynomial D, which is related to $\det(1+m)$, is given by

$$D=\left[\frac{\gamma_1}{\Gamma}(x+\alpha)-i\Omega q_1^2\right]\left[\frac{\gamma_2}{\Gamma}\left[\frac{1}{q_1}-\frac{1}{q_2}\right]^2+\left[1-\frac{i}{q_1}\right]^2+\frac{(1+ix)}{q_1^2}\right]+(x+\alpha)\left[(1+ix)\left[1+\frac{\gamma_2}{\Gamma q_2^2}\right]+\frac{\gamma_2}{\Gamma}\left[1-\frac{i}{q_2}\right]^2\right] \ . \qquad (4.4)$$

The four-wave–mixing signal is proportional to $|S(x)|^2$ whereas the susceptibility $\chi^{(3)}$ for the four-wave mixing is proportional to $S(x)$. The spectral features of $S(x)$ depend on various system parameters such as the spontaneous-emission rates γ_1 and γ_2, Fano asymmetry parameters q_1 and q_2, the strength of the pump field at ω_1, and the detuning parameter α. It is quite remarkable that the numerator in (4.3) does not depend on γ's. This is because all the recombination effects have been included in the theory. Before we discuss the general features we examine several special cases and establish contact with the results already known in literature.

A. Weak field $\Omega \ll 1$ and negligible spontaneous emission

The conventional treatment of four-wave mixing assumes that the field at ω_1 is also weak and ignores spontaneous emission. In such a case one finds

$$S(x)=\frac{\sqrt{\Omega}q_1}{(x+\alpha)}\frac{1-\dfrac{i}{q_1}-\dfrac{i}{q_2}+\dfrac{ix}{q_1q_2}}{1+ix}\ , \tag{4.5}$$

which agrees with the result of Armstrong and Beers.[3] The line shapes corresponding to (4.5) are well known.[2,3]

B. Field with arbitrary strength but with $\gamma_1=\gamma_2\approx 0$

Another important case treated in detail by Crance and Armstrong[5] is when the laser field at ω_1 could be of arbitrary magnitude. They ignored the recombination effects though dampings were included in a phenomenological manner. The recombination effects can be ignored[11] if $\gamma/\Gamma q^2 \ll 1$. Their model of damping is different from ours since they considered the decay of, for example, the level $|a\rangle$ to some other level rather than to $|i\rangle$ or $|g\rangle$. In our model we not only consider the decay of the unperturbed continuum but also "recycle" the system, i.e., the system decays back to $|i\rangle$, for example, and gets raised to the levels $|a\rangle$ and $|\epsilon\rangle$ by the interaction with the coherent driving field.

Let us assume that the spontaneous emission is negligible $\gamma_1 \sim \gamma_2 \approx 0$. In such a case $S(x)$ reduces to

$$S(x)=\frac{\sqrt{\Omega}q_1\left[1-\dfrac{i}{q_1}-\dfrac{i}{q_2}+\dfrac{ix}{q_1q_2}\right]}{(x+\alpha)(1+ix)-i\Omega q_1^2\left[\left[1-\dfrac{i}{q_1}\right]^2+\dfrac{(1+ix)}{q_1^2}\right]}\ . \tag{4.6}$$

The polynomial that appears in the denominator of (4.6) is precisely the polynomial that appears in the studies of the laser-induced autoionization[7,9] without any spontaneous emission effects. Such a polynomial is known to have the root $x=q_1$ for the case when confluence[7,9] takes place, i.e., when

$$\Omega=1+\alpha/q_1\ . \tag{4.7}$$

We thus find that $S(x)$ will have a spike for values of the field intensities corresponding to (4.7). This, in turn, implies that for such values one will have a very efficient four-wave mixing.[13] Our analysis thus shows the importance of the confluence in the determination of the efficiency of four-wave mixing. Of course the spontaneous emission γ_2 cannot be completely ignored, for even a very small value of γ_2 is going to affect the spike height considerably. For very small γ_1 and γ_2, the denominators in $|S(x)|^2$ are going to be proportional to

$$|\alpha\gamma_1+\beta\gamma_2|^2 \sim |d_{ag}d_{ai}|^2\ .$$

The numerator is also at least proportional to $|d_{ag}d_{ai}|^2$ ($|d_{ai}|^2$ comes from Ω and $|d_{ag}|^2$ comes from the dipole moment at $2\omega_2+\omega_1$). Thus, near confluence, it is sufficient to have very small γ in order to have efficient four-wave mixing.

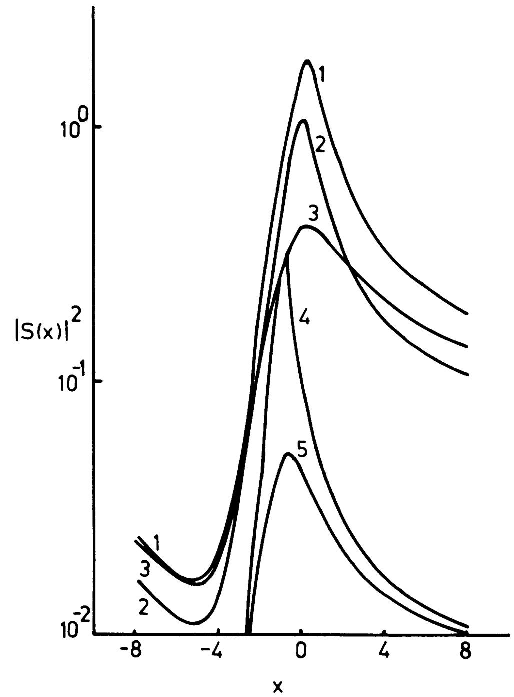

FIG. 2. Four-wave–mixing signal $|[S(x)(x+\alpha)/\sqrt{\Omega}]|^2$ for weak fields as a function of $x=(2/\Gamma)(\epsilon_a-\omega_1-2\omega_2)$ for the relaxation rates in units of Γ (1) $\gamma_1=\gamma_2=0$, (2) $\gamma_1=\gamma_2=0.1$, (3) $\gamma_1=0$, $\gamma_2=1$, (4) $\gamma_1=1$, $\gamma_2=0$, and (5) $\gamma_1=\gamma_2=1$.

As noted earlier by Agarwal *et al.*, the spontaneous-emission changes the photoelectron profiles in an important way. The four-wave–mixing profiles depend on γ_1 and γ_2 because the denominator in (4.3) is γ dependent. The width of the roots is critically dependent on γ_1 and γ_2. In the special case when $\gamma_2 \sim 0$, the polynomial $D(x)=P(-x)$ of Ref. 11. Hence the roots of $D(x)$ can be obtained from Figs. 4(b) and 5 of Ref. 11. The results of our numerical computations are displayed in Figs. 2–4. In Fig. 2 we show the effect of spontaneous emission in the two channels on the four-wave–mixing signals when the field on the transition $|i\rangle \rightarrow |a\rangle$ is weak. The spontaneous emission leads to a considerable change in the profiles. In particular, one observes a shift in the peak position as one changes γ_1 and γ_2. The changes in the peak position can be understood from an examination of the denominator D [Eq. (4.4)], which in the limit of $\Omega \rightarrow 0$ reduces to

$$D \to (x+\alpha)\left[1+\frac{\gamma_2}{\Gamma q_2^2}+\frac{\gamma_1}{\Gamma q_1^2}\right]\left\{1+ix+\left[1+\frac{\gamma_2}{\Gamma q_2^2}+\frac{\gamma_1}{\Gamma q_1^2}\right]^{-1}\left[\frac{\gamma_2}{\Gamma}\left[1-\frac{i}{q_2}\right]^2+\frac{\gamma_1}{\Gamma}\left[1-\frac{i}{q_1}\right]^2 +\frac{\gamma_1\gamma_2}{\Gamma^2}\left[\frac{1}{q_1}-\frac{1}{q_2}\right]^2\right]\right\}. \tag{4.8}$$

The expression (4.8) shows how the widths and shifts depend on γ_1, γ_2, q_1, and q_2. Figure 3 shows the behavior of the four-wave–mixing signals for the field strengths in the vicinity of confluence[9,7] [Eq. (4.7)]. For $\gamma_1=\gamma_2\approx 0$, one finds a very narrow spike. For such values of the field strengths the four-wave–mixing signal is very sensitive to the values of γ_1 and γ_2 as the various curves demonstrate. The curves also show that the dependence on γ_2 is more dramatic than on γ_1. Furthermore, for a fixed γ_2, increase of γ_1 leads to an increase in the four-wave–mixing signals. The relatively stronger dependence on γ_2 can be understood by remembering that the calculations are done to the lowest order in the two-photon transition rate $|g\rangle \leftrightarrow |i\rangle$. The position of the spike is consistent with the complex zero (4.4) corresponding to the smaller imaginary part. From the foregoing material it is clear that in order to have very efficient four-wave mixing, we have to choose systems and/or autoionizing states such that the spontaneous emission is negligibly small. Finally Fig. 4 gives the behavior of the four-wave–mixing signal for values of the field strengths away from confluence. Even here the spontaneous emission in each channel has significant effect on the strength of the signal generation. It may be noted that for the parameters used in these figures, the peak corresponding to the second zero of (4.4) is not seen as it lies in the tail of such curves. The doublet structure of the four-wave–mixing signal can be seen only for large values of q_1 and q_2 (cf. Ref. 5).

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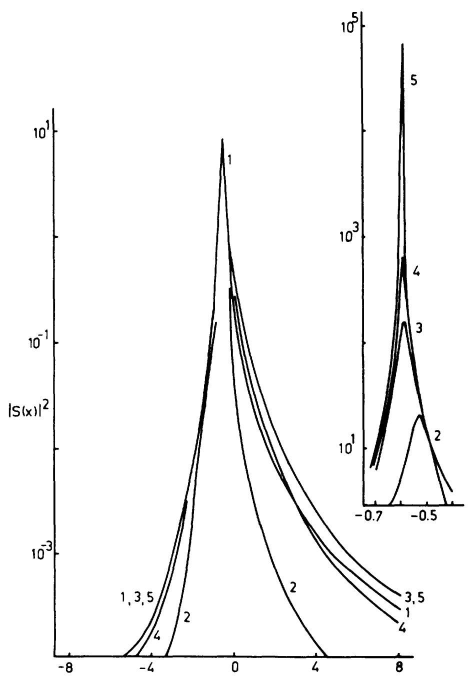

FIG. 3. Signal $|S(x)|^2$ for field strengths close to the confluence values $\Omega=0.15$, $\alpha=0.5$, $q_1=-0.6$, $q_2=-3.5$, and for γ_1 and γ_2 equal to (1) $\gamma_1=0$, $\gamma_2=1$, (2) $\gamma_1=1$, $\gamma_2=0$, (3) $\gamma_1=\gamma_2=0.1$, and (4) $\gamma_1=0.1$, $\gamma_2=0$, and (5) $\gamma_1=\gamma_2=0$. The inset gives the behavior of the spike.

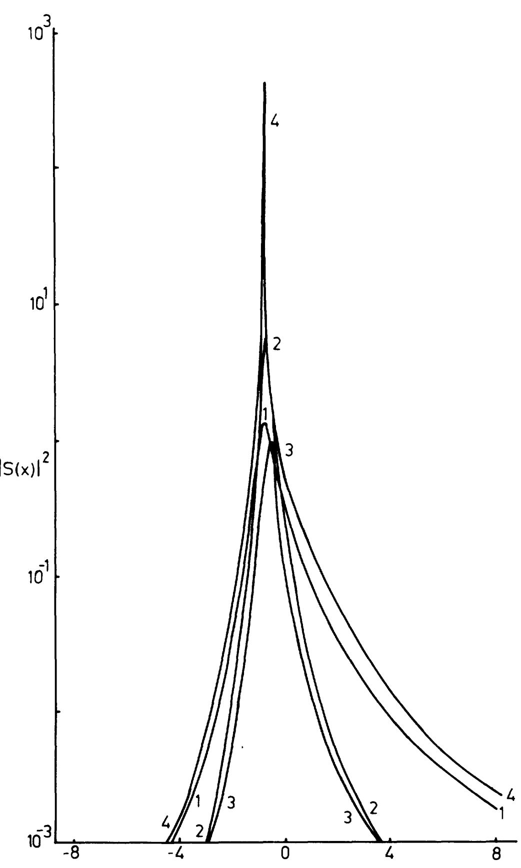

FIG. 4. Same as in Fig. 3 but for $\Omega=1$ and for the following values of γ_1 and γ_2: (1) $\gamma_1=0$, $\gamma_2=1$, (2) $\gamma_1=1$, $\gamma_2=0$, (3) $\gamma_1=\gamma_2=1$, and (4) $\gamma_1=\gamma_2=0$.

APPENDIX: SOLUTION OF (3.6) AND (3.7)

In this appendix we derive the general solution of (3.6) and (3.7) subject to the initial condition $\psi_i(0)=1$, $\psi_\epsilon(0)=0$. On taking the Laplace transform of (3.6) and (3.7) and using the initial conditions we get the following integral equation for the Laplace transform of ψ_ϵ:

$$\hat{\psi}_{\epsilon_1}+\int d\epsilon \sum_i K_i(\epsilon_1)L_i(\epsilon)\hat{\psi}(\epsilon)=-iK_1(\epsilon_1)\ , \tag{A1}$$

where

$$K_1(\epsilon_1)=\frac{v_{\epsilon_1 i}}{z(z+i\Delta_{\epsilon_1 i})}\ ,\quad L_1(\epsilon)=v^*_{\epsilon i}\ ,$$

$$K_2(\epsilon_1)=\left[\frac{\gamma_1}{2}\right]^{1/2}\frac{B^*_{\epsilon_1 a}}{(z+i\Delta_{\epsilon_1 i})}\ ,$$

$$L_2(\epsilon)=\left[\frac{\gamma_1}{2}\right]^{1/2}B_{\epsilon a}\ , \tag{A2}$$

$$K_3(\epsilon_1)=\left[\frac{\gamma_2}{2}\right]^{1/2}\frac{C^*_{\epsilon_1 a}}{(z+i\Delta_{\epsilon_1 i})}\ ,$$

$$L_3(\epsilon)=\left[\frac{\gamma_2}{2}\right]^{1/2}C_{\epsilon a}\ .$$

The integral equation (A1) has a separable kernel and, hence, can be solved by using the standard methods. The final solution can be written as

$$\hat{\psi}_i=\int d\epsilon\, L_i(\epsilon)\hat{\psi}(\epsilon)$$

$$=\sum_j[(\underline{1}+\underline{m})^{-1}]_{ij}(-i)m_{j1}\ , \tag{A3}$$

$$\hat{\psi}(\epsilon)=-iK_1(\epsilon)-\sum_i K_i(\epsilon)\hat{\psi}_i$$

$$=-i\sum_i K_i(\epsilon)[(\underline{1}+\underline{m})^{-1}]_{i1}\ . \tag{A4}$$

In Eqs. (A3) and (A4), m is a 3×3 matrix with elements

$$m_{ij}=\int d\epsilon\, L_i(\epsilon)K_j(\epsilon)\ . \tag{A5}$$

The matrix elements of m can be evaluated depending on the structure of the continuum. In what follows we assume a flat structure for the unperturbed continuum. Calculation of the integral by contour integration leads to

$$m_{11}=\frac{2\,|\vec{d}_{ia}\cdot\vec{E}\,|^2}{z\gamma_1}m_{22}\ ,$$

$$m_{jj}=\left[\frac{\gamma_{j-1}}{\Gamma}\right]\left[\frac{\left[1-\dfrac{i}{q_{j-1}}\right]^2}{\left[\dfrac{2z}{\Gamma}+1-i\alpha\right]}+\frac{1}{q_{j-1}^2}\right]\ ,\quad j=2,3$$

$$m_{23}=m_{32}=\frac{\sqrt{\gamma_1\gamma_2}}{\Gamma}\left[\frac{\left[1-\dfrac{i}{q_1}\right]\left[1-\dfrac{i}{q_2}\right]}{\left[\dfrac{2z}{\Gamma}+1-i\alpha\right]}+\frac{1}{q_1q_2}\right]\ , \tag{A6}$$

$$\frac{V^*_\epsilon}{\tilde{v}^*_{\epsilon i}}m_{12}=\frac{m_{21}zV_\epsilon}{\tilde{v}_{\epsilon i}}=\left[\frac{\gamma_1}{2}\right]^{1/2}q_1\left[\frac{\left[1-\dfrac{i}{q_1}\right]^2}{\left[\dfrac{2z}{\Gamma}+1-i\alpha\right]}+\frac{1}{q_1^2}\right]\ ,$$

$$\frac{V^*_\epsilon}{\tilde{v}^*_{\epsilon i}}m_{13}=\frac{m_{31}zV_\epsilon}{\tilde{v}_{\epsilon i}}=\left[\frac{\gamma_2}{2}\right]^{1/2}q_1\left[\frac{\left[1-\dfrac{i}{q_1}\right]\left[1-\dfrac{i}{q_2}\right]}{\left[\dfrac{2z}{\Gamma}+1-i\alpha\right]}+\frac{1}{q_1q_2}\right]\ ,$$

where

$$\Gamma=2\pi\,|V_\epsilon|^2,\ \alpha=\left[\frac{2}{\Gamma}\right](\omega_1+\epsilon_i-\epsilon_a)\ . \tag{A7}$$

Here $\tilde{v}_{\epsilon i}$ is the matrix element of the dipole interaction between the unperturbed continuum $|\epsilon)$ and the state $|i\rangle$ and can be related to the previously defined parameter[7]

$$\Omega = 2\pi \,|\, \tilde{v}_{\epsilon i} \,|^2 / \Gamma \tag{A8}$$

which is a measure of the laser field coupling between $|\, i \rangle$ and $|\, \epsilon)$. On using (A8) we can rewrite m_{11} as

$$m_{11} = \frac{\Omega q_1^2}{z} m_{22} \left[\frac{\Gamma}{\gamma_1} \right] \left[\frac{\Gamma}{2} \right] . \tag{A9}$$

For completeness we also list the value of $\det(\underline{1} + \underline{m})$:

$$\det(\underline{1} + \underline{m}) = \left[\frac{\gamma_1}{\Gamma} + \frac{\Omega q_1^2 \Gamma}{2z} \right] \left[\frac{\left[1 - \frac{i}{q_1} \right]^2}{\frac{2z}{\Gamma} + 1 - i\alpha} + \frac{1}{q_1^2} + \frac{\gamma_2 \left[\frac{1}{q_1} - \frac{1}{q_2} \right]^2}{\Gamma \left[\frac{2z}{\Gamma} + 1 - i\alpha \right]} \right] + 1 + \frac{\gamma_2}{\Gamma} \left[\frac{\left[1 - \frac{i}{q_2} \right]^2}{\left[\frac{2z}{\Gamma} + 1 - i\alpha \right]} + \frac{1}{q_2^2} \right] , \tag{A10}$$

which will be seen in Sec. IV to determine the characteristics of the four-wave—mixing signal.

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