Quantum theory of the competition between multiphoton ionization and third-harmonic generation

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A quantum-mechanical formulation for the generation of third-harmonic radiation in an atomic medium undergoing three-photon resonant multiphoton ionization is given. The generation of the third harmonic is treated as a cooperative emission and its pressure dependence is shown to be in agreement with experiments. The formulation is general enough to include both transient and steady-state phenomena and includes both traveling-wave and standing-wave cases. A comparison of the results of the present theory with those of Jackson and Wynne is given.

I. INTRODUCTION

Aron and Johnson while working at pressures higher than 1 Torr some years ago observed[1] the absence of three-photon resonant, five-photon ionization mediated by the 6*S* excited state of Xe atoms. The experiment was repeated by Miller *et al.*,[2] who not only confirmed the observation of Aron and Johnson but also showed that at low pressures, the resonant multiphoton ionization dominates whereas at high pressures the third-harmonic generation is dominant. Further evidence for the competition between the third-harmonic generation (THG) and multiphoton ionization (MPI) was provided by Glownia and Sander[3] who used circularly polarized counterpropagating beams to suppress the third-harmonic generation. Jackson and Wynne[4] very recently also demonstrated the presence of the resonantly enhanced multiphoton ionization signal even at high pressures provided one used standing waves in the experiment. Several theoretical models[4–6] have been proposed to explain the results of the observations some of which make use of the cooperative behavior[5] of the system (along the lines of superfluorescence) whereas others consider the interference[4] in the two channels involving the pumping process and the reaction back of the generated third harmonic. The approaches used so far appear to be completely disjoint. In the present paper we present a unified formulation which is sufficiently general to include all the collective effects and which in the steady state can lead to the results obtained by using the formulation of nonlinear optics. Our formulation follows very closely the one used in connection with the quantum theory of superfluorescence.[7–10]

In Sec. II we derive the basic quantum dynamical equations which describe the behavior of an atomic system under three-photon resonant pumping and the condition that the photons at 3ω can be generated once the atoms have been pumped into the excited state. The process of the third-harmonic generation has been treated as a cooperative process. The basic equations can be used in a number of situations and under a variety of initial conditions. In Sec. III we solve the dynamical equations of Sec. II under steady-state conditions. Using these solutions we study the competition between multiphoton ionization and third-harmonic generation. We consider both traveling- and standing-wave cases. The connection of our results with those of Jackson and Wynne[4] is given.

II. DYNAMICAL EQUATIONS FOR THIRD-HARMONIC GENERATION UNDER THREE-PHOTON RESONANT PUMPING

Consider a system of N multilevel atoms interacting with a field $\vec{\mathscr{E}}(x,t)$,

$$\begin{aligned}\vec{\mathscr{E}}(x,t)=&\vec{\mathscr{E}}_R^{\,+}(\tau_R)e^{i(kx-\omega t)}+\vec{\mathscr{E}}_R^{\,-}(\tau_R)e^{-i(kx-\omega t)}\\&+\mu\vec{\mathscr{E}}_L^{\,+}(\tau_L)e^{-i(kx+\omega t)}\\&+\mu\vec{\mathscr{E}}_L^{\,-}(\tau_L)e^{i(kx+\omega t)}\ .\end{aligned}\tag{2.1}$$

The field is considered to have spatial variation in one dimension. The frequency ω and the wave vector k inside the atomic medium will be related by

$$k^2=\frac{\omega^2}{c^2}\epsilon_1,\ \ \epsilon_1=\epsilon(\omega)\ ,\tag{2.2}$$

where $\epsilon(\omega)$ is the dielectric function of the atomic vapor at the frequency ω. In Eq. (2.1), $\vec{\mathscr{E}}^{\pm}$ represent the slowly varying envelopes of the input fields. The subscripts R and L represent, respectively, the waves traveling to the right and to the left. The arguments τ_R,τ_L represent, respectively, the local times, i.e., $\tau_R=t-x/v,\tau_L=(t+x/v)$. The superscripts $\pm$ represent the positive and the negative frequency parts. The form (2.1) is appropriate for both traveling and standing waves, for example $\mu=0$ ($\mu=1$) represents traveling (standing) waves. Let the two atomic levels $|g\rangle$ and $|R\rangle$ be nearly resonant with three photons of the incident laser light, i.e., $\omega_{Rg}\approx 3\omega$. The resonant three-photon process between the levels $|g\rangle$ and $|R\rangle$ and going through a series of virtual levels can be described by an effective two-level Hamiltonian[11] (or by optical Bloch equations)

$$H_{\text{eff}}=i\hbar \underline{k}_{Rg} \vdots \mathscr{E}^{+}\mathscr{E}^{+}\mathscr{E}^{+}|R\rangle\langle g|+\text{H.c.}\,, \tag{2.3}$$

where k_{Rg} is a tensor of rank three given by

$$\underline{k}_{Rg}=-\frac{1}{i\hbar^3}\sum\frac{(\vec{d})_{Rj}(\vec{d})_{ji}(\vec{d})_{ig}}{(\omega_{jg}-2\omega)(\omega_{ig}-\omega)} \tag{2.4}$$

and where $(\vec{d})_{\alpha\beta}$, as usual, represents the dipole matrix element. The Bloch equations can be obtained by introducing the spin angular momentum operators $S_\mu^{\pm}, S_\mu^z$ for each atom:

$$\begin{aligned} &S_\mu^+=|R\rangle_{\mu\mu}\langle g|\,,\quad S_\mu^-=|g\rangle_{\mu\mu}\langle R|\,,\\ &S_\mu^z=\tfrac{1}{2}(|R\rangle_{\mu\mu}\langle R|-|g\rangle_{\mu\mu}\langle g|)\,,\\ &[S_\mu^+,S_\nu^-]=2S_\mu^z\delta_{\mu\nu},\quad [S_\mu^z,S_\nu^{\pm}]\pm\delta_{\mu\nu}S_\mu^{\pm}\,. \end{aligned} \tag{2.5}$$

Since eventually we will go over to a continuum description it is convenient to introduce the current density operators and their commutation relations[7]

$$J_\alpha(\vec{x})=\sum_\mu S_\mu^\alpha\delta(\vec{x}-\vec{x}_\mu)\,, \tag{2.6}$$

$$\begin{aligned} &[J_+(\vec{x}),J_-(\vec{x}\,')]=2\delta(\vec{x}-\vec{x}\,')J_z(\vec{x})\,,\\ &[J_z(\vec{x}),J_\pm(\vec{x}\,')]=\pm\delta(\vec{x}-\vec{x}\,')J_\pm(\vec{x})\,. \end{aligned} \tag{2.7}$$

The unperturbed atomic Hamiltonian will be

$$H_A=\int d^3x\,\hbar\omega_{Rg}J_z(\vec{x})=\sum_\mu \hbar\omega_0 S_\mu^z,\quad \omega_0=\omega_{Rg}\,. \tag{2.8}$$

We next consider the generation of the third harmonic in the $\Delta l=\pm 1$ transition. Let E_T be the quantum-mechanical third-harmonic field generated by the medium. The interaction of this field with the medium is given by

$$H_T=((\vec{d}\,')_{Rg}\cdot\vec{E}^{+}_{Ti\hbar}|R\rangle\langle g|+\text{H.c.}))\,,\quad i\hbar d'_{Rg}=-d_{Rg}\,. \tag{2.9}$$

While studying the competition between the multiphoton ionization and the third-harmonic generation, we will have to treat $E_T^{(+)}$ as a dynamical variable, i.e., we have to incorporate the possibility of E_T reacting back on the medium. We will see that the conditions under which this reaction is important, would precisely be the ones for which the interference between MPI and THG is strongest. Since the field E_T is generated by the resonant absorption of three photons from the field (2.1) it is clear that E_T will have the structure

$$\begin{aligned} \vec{E}_T(x,t)=\;&\vec{\mathscr{E}}^{\,+}_{R3}(x,t)e^{i(3kx-3\omega t)}+\vec{\mathscr{E}}^{\,-}_{R3}(x,t)e^{-i(3kx-3\omega t)}+\mu\vec{\mathscr{E}}^{\,+}_{L3}(x,t)e^{-i(3kx+3\omega t)}\\ &+\mu\vec{\mathscr{E}}^{\,-}_{L3}(x,t)e^{i(3kx+3\omega t)}+\mu\vec{\mathscr{E}}^{\,+}_{R1}(x,t)e^{i(kx-3\omega t)}+\mu\vec{\mathscr{E}}^{\,-}_{R1}(x,t)e^{-i(kx-3\omega t)}\\ &+\mu\vec{\mathscr{E}}^{\,+}_{L1}(x,t)e^{-i(kx+3\omega t)}+\mu\vec{\mathscr{E}}^{\,-}_{L1}(x,t)e^{i(kx+3\omega t)}\,. \end{aligned} \tag{2.10}$$

The appearance of the terms involving $e^{\pm i(kx\pm 3\omega t)}$ should be noted. Such terms will contribute in an important manner in the standing-wave case.

The interaction Hamiltonian of the atomic system and the fields will now be sum of (2.3), (2.9), and (2,8). By using these and the definition of the current operators, the Heisenberg equations for such operators can be written down

$$\begin{aligned} \frac{\partial}{\partial t}J_-(x,t)=&-i(\omega_0+\Delta_s)J_-(x,t)+2\vec{E}_T^{\,+}\cdot\vec{d}\,'_{Rg}J_z(x,t)\\ &+2\underline{k}_{Rg}\vdots\mathscr{E}^{+}\mathscr{E}^{+}\mathscr{E}^{+}J_z(x,t)\,, \end{aligned} \tag{2.11}$$

$$\begin{aligned} \frac{\partial}{\partial t}J_z(x,t)=&-J_+(x,t)\{\vec{E}_T^{\,+}\cdot\vec{d}\,'_{Rg}\\ &+\mathscr{E}^{+}\mathscr{E}^{+}\mathscr{E}^{+}\vdots\underline{k}_{Rg}\}+\text{H.c.} \end{aligned} \tag{2.12}$$

In deriving these equations, the rotating wave approximation has been made. In Eq. (2.11) Δ_s is the field-dependent Stark shift given by

$$\begin{aligned} &\Delta_s=\underline{\chi}(\omega)\cdot\mathscr{E}^{+}\mathscr{E}^{-}\,,\\ &\underline{\chi}(\omega)=\underline{\chi}^{(g)}(\omega)+\underline{\chi}^{(R)}(\omega)\,,\\ &\underline{\chi}^{(i)}(\omega)=\frac{2}{\hbar}\sum_j\frac{(-\vec{d})_{ij}(-\vec{d})_{ji}\omega_{ji}}{(\omega_{ji}^2-\omega^2)}\,. \end{aligned} \tag{2.13}$$

The Heisenberg equations (2.11) and (2.12) can be generalized to include the transverse and longitudinal relaxation constants. Of these the transverse relaxation is very important as it can account for phase changing collisions. In order to maintain the equal time commutation relations, we have to add fluctuating forces[8] whence (2.11) is modified to

$$\begin{aligned} \frac{\partial}{\partial t}J_-(x,t)=&-\left[i(\omega_0+\Delta_s)+\frac{1}{T_2}\right]J_-(x,t)\\ &+2\vec{E}_T^{\,+}\cdot\vec{d}\,'_{Rg}J_z(x,t)\\ &+2\underline{k}_{Rg}\vdots\mathscr{E}^{+}\mathscr{E}^{+}\mathscr{E}^{+}J_z(x,t)+F_-(x,t)\,. \end{aligned} \tag{2.14}$$

The operator fluctuating force F_- has the properties

$$\begin{aligned} &\langle F_-(x,t)\rangle=0\,,\\ &\langle F_-(x,t)F_-^\dagger(x',t')\rangle=\frac{2}{T_2}\delta(x-x')\delta(t-t')\,,\\ &\langle F_-^\dagger(x,t)F_-(x',t')\rangle=0\,. \end{aligned} \tag{2.15}$$

Equation (2.12) gets similarly modified due to both T_1 relaxation and the ionization from $|R\rangle$.

The dynamical evolution of the field $\vec{E}_T$ is described by

$$\left[\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\vec{E}_T=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}(x,t)\ , \tag{2.16}$$

where $\vec{P}$ is the polarization operator at the frequency 3ω and it contains contributions from both linear and the nonlinear properties of the medium. Since $\vec{E}$ is transverse, the polarization that appears in (2.16) is also the transverse part of the polarization operator. The equations for the envelope functions, that appear in (2.10), can be obtained by substituting (2.10) in (2.16). The set of Eqs. (2.11)–(2.16) are our basic equations determining the behavior of our gaseous medium under the condition of three-photon resonant pumping. These are valid for arbitrary initial fields and for arbitrary initial conditions. Such equations will be seen to give the generation of the field at the third harmonic starting from the initial vacuum state of the third-harmonic field. The competition between MPI and THG can be studied now since the MPI signal will be proportional to the change of the population in the excited state, which in turn will be proportional to the $\langle J_-(x,t)\rangle$. In the next section we deal with the steady-state problem and comment briefly on the transient problem at the end of this section.

In order to make the equations tractable, we now smooth the fields by averaging[7,9] over transverse slices of the active volume with thickness $\Delta x \ll \lambda$. Assume a cylindrical shape of the sample with length l in the direction of propagation of the laser light, and diameter d such that $\lambda \ll d \ll l$ and Fresnel number $d^2/\lambda l \approx 1$. We further assume that the incident field is weak so that the system has a very small inversion. In such a case equations for J_z and J_x can be linearized. Keeping the particular form of the fields in view, we write $J_-(x,t)$ as

$$J_-(x,t)=e^{3ikx-3i\omega t}R_3^- +\mu L_1^- e^{-ikx-3i\omega t} +\mu L_3^- e^{-3ikx-3i\omega t}+\mu R_1^- e^{ikx-3i\omega t} \tag{2.17}$$

and a similar form for the fluctuating force F_-. The operator R_3^- (L_1^-) represents the slowly varying part of the polarization operator $J_-(x,t)$, that is traveling to the right (left) having its spatial component at the wave vector $3k$ (k). The operators L_3^- (R_1^-) have similar meanings. Using now Eqs. (2.11)–(2.17), we obtain the following equations for the field envelopes and the operators $R^{\pm},L^{\pm}$:

$$\frac{\partial}{\partial t}R_3^- =-\left[\frac{1}{T_2}+i(\delta+\Delta_s)\right]R_3^- +2J_0\vec{d}\,'_{Rg}\cdot\vec{\mathscr{E}}_{R3}^{+}+2J_0\underline{k}_{Rg}\vdots\vec{\mathscr{E}}_R^{+}\vec{\mathscr{E}}_R^{+}\vec{\mathscr{E}}_R^{+}+F_{R3}^- \ , \tag{2.18}$$

$$\mu\frac{\partial}{\partial t}L_3^- =-\left[\frac{1}{T_2}+i(\delta+\Delta_s)\right]\mu L_3^- +2J_0\vec{d}\,'_{Rg}\cdot\vec{\mathscr{E}}_{L3}^{+}+2J_0\underline{k}_{Rg}\vdots\mu^3\vec{\mathscr{E}}_L^{+}\vec{\mathscr{E}}_L^{+}\vec{\mathscr{E}}_L^{+}+\mu F_{L3}^- \ , \tag{2.19}$$

$$\mu\frac{\partial}{\partial t}R_1^- =-\left[\frac{1}{T_2}+i(\delta+\Delta_s)\right]\mu R_1^- +2J_0\vec{d}\,'_{Rg}\cdot\vec{\mathscr{E}}_{R1}^{+}\mu+2J_0\underline{k}_{Rg}\vdots 3\mu\vec{\mathscr{E}}_R^{+}\vec{\mathscr{E}}_R^{+}\vec{\mathscr{E}}_L^{+}+\mu F_{R1}^- \ , \tag{2.20}$$

$$\mu\frac{\partial}{\partial t}L_1^- =-\left[\frac{1}{T_2}+i(\delta+\Delta_s)\right]\mu L_1^- +2J_0\vec{d}\,'_{Rg}\cdot\mu\vec{\mathscr{E}}_{L1}^{+}+2J_0\underline{k}_{Rg}\vdots 3\mu^2\vec{\mathscr{E}}_R^{+}\vec{\mathscr{E}}_L^{+}\vec{\mathscr{E}}_L^{+}+\mu F_{L1}^- \ , \tag{2.21}$$

$$\left[-9k^2+\frac{9\omega^2}{c^2}+6ik\frac{\partial}{\partial x}+\frac{6i\omega}{c^2}\frac{\partial}{\partial t}\right]\mathscr{E}_{R3}^{+}=+\frac{4\pi i\hbar d_{Rg}^{*\prime}9\omega^2}{c^2}R_3^- \ , \tag{2.22}$$

$$\left[-9k^2+\frac{9\omega^2}{c^2}-6ik\frac{\partial}{\partial x}+\frac{6i\omega}{c^2}\frac{\partial}{\partial t}\right]\mathscr{E}_{L3}^{+}=+\frac{4\pi i\hbar d_{Rg}^{*\prime}9\omega^2}{c^2}L_3^- \ , \tag{2.23}$$

$$\left[-k^2+\frac{9\omega^2}{c^2}+2ik\frac{\partial}{\partial x}+\frac{6i\omega}{c^2}\frac{\partial}{\partial t}\right]\mathscr{E}_{R1}^{+}=+\frac{4\pi i\hbar d_{Rg}^{*\prime}9\omega^2}{c^2}R_1^- \ , \tag{2.24}$$

$$\left[-k^2+\frac{9\omega^2}{c^2}-2ik\frac{\partial}{\partial x}+\frac{6i\omega}{c^2}\frac{\partial}{\partial t}\right]\mathscr{E}_{L1}^{+}=+\frac{4\pi i\hbar d_{Rg}^{*\prime}9\omega^2}{c^2}L_1^- \ , \tag{2.25}$$

where

$$\delta=\omega_{Rg}-3\omega\ . \tag{2.26}$$

For the ground-state problem we will put $J_0=-n/2$, where n is the density of atoms $n=4N/\pi d^2 l$. The intensity of the third harmonic will be determined from the expectation values like $\langle \mathscr{E}_3^- \mathscr{E}_3^+ \rangle$.

To appreciate the meaning of the various terms, we examine the solution of the above equations for the traveling-wave case. Furthermore, to keep the analysis simple, we put $k\sim\omega/c$. We will further assume that all the fields are similarly polarized so that the various fields, d_{Rg}, k_{Rg}, etc., can be treated as scalars. For the traveling-wave case we have to deal with the following equations:

$$\left[\frac{\partial}{\partial x}+\frac{1}{c}\frac{\partial}{\partial t}\right]\mathscr{E}_{R3}^{+}=bR_3^- \ , \tag{2.27}$$

$$\frac{\partial}{\partial t}R_3^- = -\Gamma R_3^- - nd_{Rg}\mathscr{E}_{R3}^+ - nk_{Rg}(\mathscr{E}_R^+)^3 + F_{R3}^- \ , \tag{2.28}$$

where

$$\Gamma = [1/T_2 + i(\delta + \Delta_s)] \ , \quad b = \frac{6\pi\hbar d_{Rg}^{*\prime}\omega}{c} \ . \tag{2.29}$$

Equations (2.27) and (2.28) are linear equations and can be solved by Laplace transform techniques. For example the Laplace transform of the field at a point x and at time t is found to be

$$\hat{\mathscr{E}}_{R3}^+(x,z) = \exp\left[-x\left[\frac{z}{c} + \frac{bnd'_{Rg}}{z+\Gamma}\right]\right]\hat{\mathscr{E}}_{R3}^+(x=0,z) + \int_0^x dx' \exp\left[-x'\left[\frac{z}{c} + \frac{bnd'_{Rg}}{z+\Gamma}\right]\right]\mathscr{E}_{R3}^+(x-x',t=0)$$
$$+ \frac{b}{z+\Gamma}\int_0^x dx' \exp\left[-x'\left[\frac{z}{c} + \frac{bnd'_{Rg}}{z+\Gamma}\right]\right]\{R_3^-(x-x',t=0) - nk_{Rg}(\hat{\mathscr{E}}_R^+)^3(x-x',z) + \hat{F}_{R3}^-(x-x',z)\} \ . \tag{2.30}$$

The form in time domain can be obtained by using the relations

$$\int_0^\infty \left(\frac{t}{a}\right)^n J_n[(4at)^{1/2}]e^{-zt}dt = \frac{1}{z^{n+1}}e^{-a/z} \ , \quad a > 0 \tag{2.31}$$

$$\int_0^\infty f(t)e^{-\Gamma t}e^{-zt}dt = \hat{f}(z+\Gamma) \ , \tag{2.32}$$

$$\int_0^\infty f(t-\beta)\theta(t-\beta)e^{-zt}dt = \hat{f}(z)e^{-\beta z} \ . \tag{2.33}$$

We may now note the relationship of the parameters that appear in (2.30) to those appearing in the theories of cooperative emission. Since the emission is at the frequency 3ω, one can define the cooperative length and "superfluorescence" time by

$$l_c^{-2} = \frac{6\pi\hbar\,|d'_{Rg}|^2\omega n}{c^2} \ , \quad \tau = l_c^2/lc \ . \tag{2.34}$$

On combining (2.29) and (2.34) we have

$$bndc = c^2/l_c^2 \ . \tag{2.35}$$

The first two terms in (2.30) will contribute only if initially the third-harmonic field is present. Since the initial state of the third-harmonic field is a vacuum state, we can drop the first two terms of (2.30) as long as we are calculating the *normally ordered* expectation values of $\mathscr{E}_{R3}^+(x,t)$. Moreover, for the calculation of such expectation values, the random operator force term F_{R3}^- does not contribute because of the property (2.15). The contribution coming from the terms R_3^- depends on the initial state of the atomic system. For the usual cooperative emission problem, the initial state is a state of complete inversion and there is no coherent driving field. Thus in that case the emission occurs because of the nonvanishing values of $\langle R_3^+(x,t=0)R_3^-(x',t=0)\rangle$. For the present problem of the third-harmonic generation, the atoms at $t=0$ are in the ground state and hence the expectation values $\langle R_3^+(x)R_3^-(x')\rangle$ also vanish. Thus in the present case the third-harmonic generation occurs due to the driving field term $(\mathscr{E}_R^+)^3$. Of course, if the initial state of the atom is a superposition of the ground and the intermediate resonant state, then THG arises from both $\langle R_3^+(x)R_3^-(x')\rangle$ and the driving field.

Assuming that the atom at $t=0$ is in the ground state, the intensity of the generated third harmonic can be written as

$$I_3(x,t) = \left|\frac{c}{l_c^2}\frac{k_{Rg}}{d'_{Rg}}\int_0^x dx'\int_0^t dt'(\mathscr{E}_R^+(x-x',t-t'))^3 e^{-\Gamma(t'-x'/c)}\theta\left[t'-\frac{x'}{c}\right]J_0\left[\frac{4c}{l_c^2}x'\left[t'-\frac{x'}{c}\right]\right]^{1/2}\right|^2 . \tag{2.36}$$

Thus the third-harmonic generation can be studied depending upon the input driving field. In the limiting cases of optically thin and thick samples and for constant input fields, we get simpler expressions

$$I_3(x,t) = \begin{cases} \left|\dfrac{c}{l_c^2}\dfrac{k_{Rg}(\mathscr{E}_R^+)^3 x}{d'_{Rg}}(1-e^{-\Gamma t})\right|^2 , & (2.37) \\ \left|\dfrac{c}{l_c^2}\dfrac{k_{Rg}(\mathscr{E}_R^+)^3}{d_{Rg}}\dfrac{1}{2\pi i}\oint\dfrac{e^{zt}dz}{z\left[z(z+\Gamma)+\dfrac{c^2}{l_c^2}\right]}\right|^2 , & (2.38) \end{cases}$$

respectively. Note that (2.37) also gives the generation of the third harmonic in the initial stages. The foregoing analysis clearly shows the role of the various initial conditions in the generation of the third-harmonic radiation.

III. MULTIPHOTON IONIZATION AND THE THIRD-HARMONIC SIGNALS IN THE STEADY STATE

In this section we discuss the various signals in the steady state. In particular we show how our model based on the collective behavior leads to the steady-state cancellation, i.e., disappearance of the multiphoton ionization signal in the traveling-wave case and to partial cancellation for the standing-wave case and thus confirming the results of Jackson and Wynne.[4] The conditions for such a cancellation are given. Our model also shows how the steady-state results depend on the density of the atomic vapor. In order to keep the analysis simple we treat the case when all the fields are similarly polarized. This enables us to treat all the fields as scalars. Similarly, d_{Rg}, k_{Rg}, etc., can be treated as scalars. In view of our discussion following Eq. (2.30), we can treat the set (2.18)—(2.25) as a c-number set for calculating the steady-state normally ordered expectation values.

In the steady state the solutions of (2.18)—(2.21) are

$$\begin{aligned} R_3^- &= -\mathscr{D} n[d'_{Rg}\mathscr{E}^+_{R3}+k_{Rg}(\mathscr{E}^+_R)^3] ,\\ \mu L_3^- &= -\mathscr{D} n[d'_{Rg}\mu\mathscr{E}^+_{L3}+k_{Rg}\mu^3(\mathscr{E}^+_L)^3] ,\\ \mu R_1^- &= -\mathscr{D} n[d'_{Rg}\mathscr{E}^+_{R1}\mu+3k_{Rg}\mu(\mathscr{E}^+_R)^2\mathscr{E}^+_L] ,\\ \mu L_1^- &= -\mathscr{D} n[d'_{Rg}\mu\mathscr{E}^+_{L1}+3\mu^2 k_{Rg}\mathscr{E}^+_R(\mathscr{E}^+_L)^2] , \end{aligned} \tag{3.1}$$

$$\mathscr{D}=\left[\frac{1}{T_2}+i(\delta+\Delta_s)\right]^{-1} . \tag{3.2}$$

Thus the current density $J_-(x,t)$ in the steady state will be

$$J_-(x,t)=-\mathscr{D} n\Big\{[d'_{Rg}\mathscr{E}^+_{R3}+k_{Rg}(\mathscr{E}^+_R)^3]e^{3ikx}+[\mu d'_{Rg}\mathscr{E}^+_{L3}+k_{Rg}\mu^3(\mathscr{E}^+_L)^3]e^{-3ikx} + [\mu d'_{Rg}\mathscr{E}^+_{R1}+3k_{Rg}\mu(\mathscr{E}^+_R)^2\mathscr{E}^+_L]e^{ikx}+[\mu d'_{Rg}\mathscr{E}^+_{L1}+3k_{Rg}\mu^2\mathscr{E}^+_R(\mathscr{E}^+_L)^2]e^{-ikx}\Big\} . \tag{3.3}$$

On substituting (3.1) in (2.22)—(2.25), we find the steady-state results for the field envelopes under the assumption that the input field envelopes are constants:

$$\mathscr{E}^+_{R3}(x,t)=\frac{-Qk_{Rg}(\mathscr{E}^+_R)^3}{d'_{Rg}P_3}(1-e^{+(i/6kl^2)P_3x}) , \tag{3.4a}$$

$$\mu\mathscr{E}^+_{L3}(x,t)=\frac{-Qk_{Rg}\mu^3(\mathscr{E}^+_L)^3}{d'_{Rg}P_3}(1-e^{-(i/6kl^2)P_3x}) , \tag{3.4b}$$

$$\mu\mathscr{E}^+_{R1}(x,t)=\frac{-3Qk_{Rg}\mu(\mathscr{E}^+_R)^2\mathscr{E}^+_L}{d'_{Rg}P_1}(1-e^{(ix/2kl^2)P_1}) , \tag{3.4c}$$

$$\mu\mathscr{E}^+_{L1}(x,t)=\frac{-3Q\mu^2k_{Rg}(\mathscr{E}^+_R)(\mathscr{E}^+_L)^2}{d'_{Rg}P_1}(1-e^{(-ixP_1/2kl^2)}) , \tag{3.4d}$$

where

$$\begin{aligned} P_\alpha &= \left[\left[\frac{9\omega^2}{c^2}-\alpha^2k^2\right]l^2+Q\right] ,\\ Q &= \frac{4\pi n\,|d_{Rg}|^2}{\hbar}\mathscr{D} i\left[\frac{3\omega l}{c}\right]^2 . \end{aligned} \tag{3.5}$$

The parameter Q can be written in terms of the susceptibility of the atomic vapor at the frequency 3ω if we retain only the resonant contribution, i.e., on writing

$$\epsilon(3\omega)-1\approx\frac{4\pi n\,|d_{Rg}|^2}{\hbar\left[\delta+\Delta_s-\frac{i}{T_2}\right]} , \tag{3.6}$$

we get

$$Q=(\epsilon_3-1)\left[\frac{3\omega l}{c}\right]^2 . \tag{3.7}$$

Now as mentioned before k and ω are related by (2.2). Since the medium is assumed to have no single photon resonance, $\epsilon(\omega)$ will contain only the nonresonant contribution and for atomic vapors the nonresonant term is extremely small and hence we can approximate $\epsilon(\omega)\approx 1$ leading to $k=\omega/c$. We will now consider the two cases corresponding to the traveling wave ($\mu=0$) and the standing wave ($\mu=1$) separately.

A. Traveling-wave case ($\mu=0$)

In this case there are no waves propagating to the left. Moreover (3.4a) reduces to

$$\mathscr{E}^+_{R3}(x,t)=\frac{-k_{Rg}(\mathscr{E}^+_R)^3}{d'_{Rg}}[1-\exp(isx-\alpha x)] , \tag{3.8}$$

where s and α are defined by

$$\begin{aligned} s &= \frac{3}{2}\left[\frac{\omega}{c}\right]\mathrm{Re}(\epsilon_3-1)\\ &= \frac{6\pi n\omega\,|d_{Rg}|^2(\delta+\Delta_s)}{\hbar c\left[\left[\frac{1}{T_2}\right]^2+(\delta+\Delta_s)^2\right]} , \end{aligned} \tag{3.9}$$

$$\begin{aligned} \alpha &= \frac{3}{2}\frac{\omega}{c}\mathrm{Im}\epsilon_3\\ &= \frac{6\pi n\omega\,|d_{Rg}|^2\left[\frac{1}{T_2}\right]}{\hbar c\left[\left[\frac{1}{T_2}\right]^2+(\delta+\Delta_s)^2\right]} . \end{aligned} \tag{3.10}$$

On substituting (3.8) in (3.3) we get the current density

$$J_{-}(x,t)=-\mathscr{D}nk_{Rg}(\mathscr{E}_R^{+})^3 e^{ix(3k+s)-\alpha x} . \qquad (3.11)$$

The coefficient α, which essentially represents the absorption of the free wave at 3ω, is density and collision dependent. Hence in the limit of the high pressure (large density), the current density $J_{-}(x,t)\approx 0$. Therefore, the MPI signal is absent since such a signal is proportional to $J_{-}(x,t)$. The strength of the generated third harmonic will be

$$|\mathscr{E}_{R3}^{+}|^2 \approx |k_{Rg}/d'_{Rg}|^2 |\mathscr{E}_R^{+}|^6 . \qquad (3.12)$$

Thus the MPI signal goes to zero due to the interference of the two amplitudes—(i) absorption of three photons described by $k_{Rg}(\mathscr{E}_R^{+})^3$, (ii) interaction of the generated third harmonic described by $d_{Rg}\mathscr{E}_{R3}^{+}$. The signal vanishes only for densities such that $\alpha x \gg 1$. A similar result for the cancellation was given by Jackson and Wynne[4] who however did not consider what happens in the low-pressure limit. It should be added that $(3k+s)\approx 3k\sqrt{\mathrm{Re}\epsilon_3}$ since $\epsilon_3 \approx 1$ and thus $(3k+s)$ is the wave vector of the free wave generated at 3ω. It is also clear when pressure and densities are such that $\alpha l \ll 1$, then the third-harmonic intensity will be quite small as it will be proportional to $\alpha^2 l^2$.

The variation of the generated third-harmonic intensity with incident wavelength has been studied by Miller and Compton at different pressures. It is clear that the peaks in their curve (Ref. 2, Fig. 4) correspond to the vanishing of the parameter s (phase matching condition). The parameter s vanishes for $\delta+\Delta_s=0$ if the resonant approximations for the dielectric functions ϵ_1 and ϵ_3 are made. If the nonresonant contributions to ϵ_1 and ϵ_3 are retained, then one has a more general condition namely $\mathrm{Re}(\sqrt{\epsilon_3}-\sqrt{\epsilon_1})=0$. Thus according to (3.8), the peak intensity is $\sim(1-e^{-ap})^2$ assuming linear dependence of nT_2 on pressure p. This pressure dependence is in agreement with the observations of Miller and Compton (Ref. 2, Fig. 5). The above plane-wave theory does not explain the dependence of the peak position on pressure. For this purpose one should really use Gaussian beams as experiments had focused beams. Thus the applied field should be taken to have the form

$$\mathscr{E}_R^{+}\to\mathscr{E}_R^{+}\frac{1}{(1+i\beta)}\exp-\frac{k\gamma^2}{b(1+i\beta)} , \quad b=k\varpi^2,\ \beta=\frac{2(x-f)}{b} , \qquad (3.13)$$

where ϖ is spot size. We have a similar expression for the generated field

$$\mathscr{E}_R^{+}\to\mathscr{E}_{R3}^{+}(x)\frac{1}{(1+i\beta)}\exp-\frac{3k\gamma^2}{b(1+i\beta)} , \qquad (3.14)$$

where γ is the component of the vector $\vec{r}$ in the yz plane. It can therefore be shown that the generated third harmonic is given by (3.8) with

$$|[1-\exp(isx-\alpha x)]|^2 \left| \left[\frac{\Delta k}{2}\right]^2 \right| F(\Delta k) , \qquad (3.15)$$

$$F(\Delta k)=\left| \int_{-2f/b}^{\beta} d\beta \frac{e^{-(ib/2)\Delta k(\beta'-\beta)}}{(1+i\beta')^2} \right|^2 . \qquad (3.16)$$

The function F has been extensively studied by Bjorklund[12] who has shown how the peak in F shifts to negative values of Δk as the parameters $b/l, f/l$ are changed. The parameter b depends on the refractive index at the fundamental frequency and that

$$\Delta kb=(\sqrt{\epsilon_3}-\sqrt{\epsilon_1})\frac{3\omega}{c}b = \frac{6\pi n\omega |d_{Rg}|^2 b}{\hbar c\left[\delta+\Delta_s-\frac{i}{T_2}\right]}=+\eta , \qquad (3.17)$$

where real and imaginary parts of η give the position and the width of F. Note that $\mathrm{Re}\eta<0$. Equation (3.17) leads to

$$\delta+\Delta_s=\frac{i}{T_2}+\frac{6\pi n\omega |d_{Rg}|^2 b}{\hbar c\eta} \qquad (3.18)$$

and hence the shift in the peak position and the peak width are proportional to pressure. The sign of the real part of η also explains the shifting of the peak towards blue as can be seen by calculating the wavelength corresponding to (3.18). It must also be added that at very low pressures, the production of coherent radiation at 3ω would be comparable to that of the incoherent radiation at 3ω, which so far has been ignored in the analysis. Moreover, at such low pressures the ratio of the single-atom MPI rate to the THG is of the order of two photon ionization rates from the excited state $|R\rangle$ per spontaneous emission at $3\omega\approx 10^{-8}-10^{-10}I^2$, where I is in $\mathrm{W/m^2}$. Hence for the intensities ($I\sim 10^{14}\ \mathrm{W/m^2}$) used in the experiments, the MPI would dominate over the THG.

B. Standing-wave case ($\mu=1$)

It has been shown experimentally and theoretically by Jackson and Wynne that the cancellation is incomplete in the standing-wave case. We will now see the consequences of our formulation in the standing-wave case ($\mu=1$). On substituting (3.4) in (3.3) we get the current density

$$\begin{aligned} J_{-}(x,t)=&-\mathscr{D}nk_{Rg}(\mathscr{E}_R^{+})^3 e^{ix(3k+s)-\alpha x}-\mathscr{D}nk_{Rg}(\mathscr{E}_L^{+})^3 e^{-ix(3k+s)+\alpha x} \\ &-3\mathscr{D}nk_{Rg}(\mathscr{E}_R^{+})^2\mathscr{E}_L^{+}\left[1-\frac{Qc^2}{8\omega^2 l^2}(1-e^{ixP_1/2kl^2})\right]e^{ikx} \\ &-3\mathscr{D}nk_{Rg}(\mathscr{E}_L^{+})^2\mathscr{E}_R^{+}\left[1-\frac{Qc^2}{8\omega^2 l^2}(1-e^{-ixP_1/2kl^2})\right]e^{-ikx} , \end{aligned} \qquad (3.19)$$

where we have approximated $P_1 \approx (9\omega^2/c^2 - k^2)l^2 = (8\omega^2/c^2)l^2$.

The expression (3.19) shows that even if we drop the free waves at the third harmonic, there is a net contribution to $J_-(x,t)$. This contribution essentially arises when two photons are absorbed from, say, the wave traveling to the right and one photon is absorbed from the wave traveling to the left. Since $J_-(x,t)$ is finite in the standing-wave case, the resonantly enhanced MPI signal survives even though the third harmonic continues to be generated.

In summary we have shown how a very general quantum-mechanical formulation of the competition between third-harmonic generation and multiphoton ionization can be given. The formalism is valid under a variety of excitation and initial conditions involving both traveling and standing waves as well as pulses. In the steady state and in the limit of large pressure, our results agree with those of Jackson and Wynne obtained by using the formulation of nonlinear optics. The pressure dependence of the generated third harmonic is found to be in agreement with the observations of Miller and Compton.[2]

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