Polarization Renormalization Due to Nonlinear Optical Generation

J. J. Wynne
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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By concentrating on the *total* electric polarization at the frequency of a wave generated by a coherent nonlinear optical process, the author extends the treatment of Bloembergen and Pershan to show that anomalously small multiphoton excitation is a consequence solely of Maxwell's equations, with no recourse to a quantum mechanical treatment of the nonlinear medium's polarization response to applied electric fields.

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The seminal work of Bloembergen and his colleagues[1,2] codified the theory of nonlinear optics and laid a systematic framework for the analysis of a large fraction of the experimental results that followed. In particular, Bloembergen and Pershan (BP)[1] solved the electromagnetic (em) wave equation with a nonlinear source electric polarization ($P^{\rm NLS}$), showing how the solution for an em wave propagating in a nonlinear medium could be described as a superposition of a driven wave (driven by $P^{\rm NLS}$) and a free wave. Their results have been widely accepted and used to calculate the electric *field* amplitude of em waves generated by coherent nonlinear optical processes. However, relatively little attention has been paid to a complementary aspect, namely, the electric *polarization* amplitude at the frequency of the generated em wave, since experimental measurements of this polarization have been very rare.

Recent experiments and theory[3-6] have dealt with phenomena where coherent generation of em waves is intimately involved with multiphoton excitation, leading to unexpected results. In particular, the absence, disappearance with increasing vapor pressure, or reappearance with retroreflection of a multiphoton-ionization signal,[3] as well as the disappearance with increasing pressure of fluorescence from a multiphoton-excited state,[4] have been explained by considering the effect of coherent third-harmonic generation on the multiphoton excitation.[5,6] These explanations[5,6] present specific calculations showing that the total excitation is reduced by the harmonic generation process, but they fail to address the underlying general principle that leads to such a reduction. In this paper, I will show that this reduction is *dictated* by the laws of em wave propagation, namely, the em wave equation that is derived from Maxwell's equations. I will treat the problem entirely classically, making no recourse to a quantum mechanical description of the linear or nonlinear system response. The key idea is to consider the *total* electric polarization ($P^{\rm tot}$). This is the sum of the aforementioned *nonlinear source* polarization ($P^{\rm NLS}$) (the driving force of generation) and the *linear* polarization ($P^{\rm lin}$), i.e., the linear response of the polarizable medium to the generated electric field. Using this idea, I apply the BP approach to situations where the coherently generated em wave experiences *linear* absorption, leading to a spatial decay of the free wave, so that the spatially persisting wave is described solely by the driven-wave solution. Then, careful consideration of the relationship between $P^{\rm tot}$ and $P^{\rm NLS}$ is sufficient to explain the anomalous experimental results.[3,4]

A steady-state (in time), plane-wave approach is sufficient to demonstrate the essential physical ideas. Following BP, I consider the generation, in a homogeneous nonlinear medium, of an em wave at frequency ω_G by a transverse, linearly polarized $P^{\rm NLS}(\omega_G)$. This polarization is the response of the nonlinear medium to applied em plane waves at frequencies other than ω_G, and, as such, its spatial variation will reflect the spatial variation of those waves. I assume a traveling wave $P^{\rm NLS}(\omega_G)=P_0^{\rm NLS}\exp[i(k_Dz-\omega_Gt)]$ propagating in the z direction with a spatial periodicity given by k_D, the driven wave vector; $P_0^{\rm NLS}$ is the spatially invariant amplitude.[7] Further I assume that k_D is real, which means that there is no attenuation of the applied waves and consequently of $P^{\rm NLS}$. The electric field of the generated wave, $\mathbf{E}(\omega_G)$, is determined from the em wave equation for the Fourier component at ω_G,

$$\frac{\partial^2E(\omega_G)}{\partial z^2}+\left(\frac{\omega_G}{c}\right)^2E(\omega_G)=-4\pi\left(\frac{\omega_G}{c}\right)^2P^{\rm tot}(\omega_G). \quad (1)$$

Here, the total polarization is given by

$$P^{\rm tot}(\omega_G)=P^{\rm lin}(\omega_G)+P^{\rm NLS}(\omega_G)$$
$$=(4\pi)^{-1}[\epsilon(\omega_G)-1]E(\omega_G)+P^{\rm NLS}(\omega_G), \quad (2)$$

where the linear polarization is related to the electric field by the relationship $P^{\rm lin}(\omega_G)=\chi^{\rm lin}(\omega_G)\times E(\omega_G)$, and $\epsilon(\omega_G)=1+4\pi\chi^{\rm lin}(\omega_G)$ is the usual linear dielectric constant. Substituting Eq. (2) into Eq. (1) gives[1,2]

$$\frac{\partial^2 E(\omega_G)}{\partial z^2}+\epsilon(\omega_G)\left(\frac{\omega_G}{c}\right)^2 E(\omega_G)=-4\pi\left(\frac{\omega_G}{c}\right)^2 P^{\rm NLS}(\omega_G). \qquad (3)$$

For a semi-infinite nonlinear medium with a planar boundary at $z=0$, BP found the following solution to Eq. (3):

$$E(\omega_G)=E_D(\omega_G)+E_F\exp\{i[k(\omega_G)z-\omega_G t]\}, \quad (4)$$

where E_F is the spatially invariant amplitude coefficient of a free wave propagating at $k(\omega_G)=[\epsilon(\omega_G)]^{1/2}\omega_G/c$, and E_D is the driven wave propagating at k_D. BP gave the solution for E_D,

$$E_D(\omega_G)=4\pi P^{\rm NLS}(\omega_G)/[\epsilon_D(\omega_G)-\epsilon(\omega_G)], \qquad (5)$$

where $\epsilon_D(\omega_G)$, the effective linear dielectric constant of the driven wave, is related to the driven wave vector by $k_D=[\epsilon_D(\omega_G)]^{1/2}\omega_G/c$.

For now, the amplitude coefficient E_F is unimportant, because I will first treat the case where linear absorption at ω_G has led to the exponential decay (in space) of the free wave. [Formally, such linear absorption results in a complex $k(\omega_G)$ and a free wave whose amplitude decays exponentially with an e-folding distance of $|\mathrm{Im}\,k|^{-1}$.] This leaves *only* the driven wave, and substituting for $E(\omega_G)$ in Eq. (2) with Eq. (5) yields

$$P^{\rm tot}(\omega_G)=\left(\frac{\epsilon_D(\omega_G)-1}{\epsilon_D(\omega_G)-\epsilon(\omega_G)}\right)P^{\rm NLS}(\omega_G). \qquad (6)$$

Clearly, the generation of the wave $E(\omega_G)$ changes $P^{\rm tot}(\omega_G)$ from its value $P^{\rm NLS}(\omega_G)$ in the absence of $E(\omega_G)$. But the *specific* value taken on by $P^{\rm tot}(\omega_G)$ when $E(\omega_G)=E_D(\omega_G)$ is just that required for an undamped em wave propagating with wave vector k_D. Another way of writing Eq. (6) is $P^{\rm tot}(\omega_G)=(4\pi)^{-1}[\epsilon_D(\omega_G)-1]E_D(\omega_G)$, which explicitly shows that the driven wave at ω_G looks just like an em plane wave propagating in a medium described by a linear dielectric constant $\epsilon_D(\omega_G)$.

An alternative description of this situation is that $P^{\rm NLS}(\omega_G)$ is *renormalized* to a new value, $P^{\rm tot}(\omega_G)$, by the generation of the field $E_D(\omega_G)$ and its accompanying $P^{\rm lin}(\omega_G)$. Under these conditions, energy is not exchanged between the driving fields [responsible for $P^{\rm NLS}(\omega_G)$] and $E_D(\omega_G)$, and $P^{\rm tot}(\omega_G)$ is in phase with $E_D(\omega_G)$ so that enery is not exchanged between the polarizable medium and the fields.[8]

Equation (6) is a general result for any nonlinear medium in which a transverse $P^{\rm NLS}(\omega_G)$ is created and a free wave at ω_G is absent, with the restriction that $P^{\rm NLS}(\omega_G)$ is not damped [i.e., $\epsilon_D(\omega_G)$ is real] and the approximation that $E_D(\omega_G)$ is sufficiently small so as not to react back on the original waves that create $P^{\rm NLS}(\omega_G)$. The magnitude of $P^{\rm tot}(\omega_G)$ might be less than, equal to, or greater than that of $P^{\rm NLS}(\omega_G)$, depending on the linear optical properties of the nonlinear medium. In particular, if $[\epsilon_D(\omega_G)-1]/[\epsilon_D(\omega_G)-\epsilon(\omega_G)]\ll 1$, $P^{\rm tot}(\omega_G)$ will be relatively small, and experimental measurements that depend on $P^{\rm tot}(\omega_G)$ will show an *anomalously* weak signal. The observation of such a weak signal is surprising[3,4] and is not explained by a simple measurement of the light intensity at ω_G. Instead, the coherent superposition and destructive interference of $P^{\rm lin}(\omega_G)$ and $P^{\rm NLS}(\omega_G)$ must be recognized as playing a critical role in allowing for a smaller magnitude for $P^{\rm tot}(\omega_G)$ than one would expect from consideration of $P^{\rm lin}(\omega_G)$ or $P^{\rm NLS}(\omega_G)$ separately.[6] The experiments[3,4] that showed anomalously small $P^{\rm tot}(\omega_G)$ were carried out in an atomic vapor where the frequencies of the input lasers [responsible for $P^{\rm NLS}(\omega_G)$] were far from resonance, while ω_G was near resonance, so that[9]

$$\frac{\epsilon_D(\omega_G)-1}{\epsilon_D(\omega_G)-\epsilon(\omega_G)}=\frac{P^{\rm tot}(\omega_G)}{P^{\rm NLS}(\omega_G)}\simeq 0.$$

It is instructive to extend this treatment to a $P^{\rm NLS}(\omega_G)$ that is the superposition of several traveling plane waves. Each plane-wave component of $P^{\rm NLS}(\omega_G)$ will produce a component of the driven field with the same spatial dependence as its source, leading to different renormalized values for each plane-wave component of $P^{\rm tot}(\omega_G)$, depending on the phase mismatch. This is illustrated by the special case of third-harmonic generation (THG) from a laser beam at frequency ω and wave vector k that is split into two waves passing through a nonlinear medium in counterpropagating directions. The forward-propagating beam (k) creates $P^{\rm NLS}(3\omega,3k)$, a nonlinear polarization plane wave propagating in the forward direction with a wave vector $3k$; the backward-propagating beam creates $P^{\rm NLS}(3\omega,-3k)$; and the cross terms between the forward- and backward-propagating beams create $P^{\rm NLS}(3\omega,k)$ and $P^{\rm NLS}(3\omega,-k)$, waves propagating with wave vector k and $-k$, respectively. For this situation, the driven-wave solution of Eq. (3) contains terms proportional to each of the nonlinear polarization waves, but the contributions from the waves with wave vector k or $-k$ have a very different amplitude from those from waves with wave vector $3k$ or $-3k$.[6] It is straightforward to show that this difference is due to the entirely different phase mismatches. The expression for $P^{\rm tot}(3\omega)$, analogous to Eq. (6), is

$$P^{\rm tot}(3\omega)=\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)-\epsilon(3\omega)}\right)[P^{\rm NLS}(3\omega,3k)+P^{\rm NLS}(3\omega,-3k)] + \left(\frac{\epsilon(\omega)/9-1}{\epsilon(\omega)/9-\epsilon(3\omega)}\right)[P^{\rm NLS}(3\omega,k)+P^{\rm NLS}(3\omega,-k)]. \tag{7}$$

In the case (discussed earlier) of an atomic vapor with 3ω near resonance and ω far from resonance, $[\epsilon(\omega)-1]/[\epsilon(\omega)-\epsilon(3\omega)]\simeq 0$, so that the contributions to $P^{\rm tot}(3\omega)$ by the waves at $3k$ and $-3k$ are still renormalized to anomalously small values; but $[\epsilon(\omega)/9-1]/[\epsilon(\omega)/9-\epsilon(3\omega)]\simeq 1$, so that the contributions by the waves at k and $-k$ are essentially *not* renormalized, leading to easily measurable effects due to $P^{\rm tot}(3\omega)$ (e.g., ionization, fluorescence, etc.).

The more general case of THG from two beams ($\vec{k}_1$ and $\vec{k}_2$) crossing at an arbitrary angle (θ) produces analogous results, whereby the nonlinear polarization waves at $3\vec{k}_1$ and $3\vec{k}_2$ are renormalized as in the first term of Eq. (7), while the nonlinear polarization waves at $2\vec{k}_1+\vec{k}_2$ and $\vec{k}_1+2\vec{k}_2$ are renormalized with a coefficient $[\frac{1}{9}\epsilon(\omega)\times(5+4\cos\theta)-1]/[\frac{1}{9}\epsilon(\omega)(5+4\cos\theta)-\epsilon(3\omega)]$. This coefficient is seen to reduce to the values already derived for copropagating beams ($\theta=0°$) and counterpropagating beams ($\theta=180°$).

The previous discussion has been restricted to the case where any free wave at ω_G has damped out (the optically thick case[6]). More generally, free waves are present, and $P^{\rm tot}(\omega_G)$ will depend on the amplitude and phase of such free waves. Returning to Eq. (4), the boundary condition at $z=0$ (the entrance to the nonlinear medium) establishes the magnitude and phase of E_F. Because of the phase mismatch, $\Delta k=k(\omega_G)-k_D$, the free wave will show spatial oscillations in phase relative to $E_D(\omega_G)$, leading to spatial oscillations in amplitude and phase of $E(\omega_G)$, corresponding spatial oscillations in $P^{\rm lin}(\omega_G)$, and complementary spatial oscillations in $P^{\rm tot}(\omega_G)$. Such oscillations will be reflected in the spatial dependence of experimental signals, such as ionization or fluorescence, that depend on $P^{\rm tot}(\omega_G)$.

A special case to consider is the most common situation for generation of a new wave at ω_G, namely, $E(\omega_G)\simeq 0$ at $z=0$. Then $E_F\exp(-i\omega_G t)\simeq -E_D(\omega_G)|_{z=0}$, which, upon substitution into Eq. (4), yields $E(\omega_G)=[1-\exp(i\Delta kz)]E_D(\omega_G)$,[10] and upon substitution into Eq. (2) gives

$$P^{\rm tot}(\omega_G)\cong\left(\frac{[\epsilon_D(\omega_G)-1]-[\epsilon(\omega_G)-1]\exp(i\Delta kz)}{\epsilon_D(\omega_G)-\epsilon(\omega_G)}\right)P^{\rm NLS}(\omega_G). \tag{8}$$

This is a generalization of Eq. (6) for $P^{\rm tot}(\omega_G)$ as a function of z, before the free wave has damped out. One sees that $P^{\rm tot}(\omega_G)$ oscillates in z with the phase factor $\exp(i\Delta kz)$. If the nonlinear medium is absorbing at ω_G, $k(\omega_G)$ and, therefore, Δk have positive imaginary parts, and $|P^{\rm tot}(\omega_G)|$ will decay in space with increasing z. For small $|\mathrm{Im}\Delta k|z$ (the optically thin case[6]), Eq. (8) shows that $P^{\rm tot}(\omega_G)/P^{\rm NLS}(\omega_G)$ has a constant amplitude but a phase that varies sinusoidally with $|\mathrm{Re}\Delta k|z$. For large $|\mathrm{Im}\Delta k|z$ (the optically thick case[6]), $\exp(i\Delta kz)\to 0$, the free wave has damped out, and Eq. (8) reduces to the asymptotic result, Eq. (6).

This paper has concentrated on a classical derivation of the renormalization of a nonlinear polarization in the presence of coherent nonlinear optical generation. The goal has been to explain the results of Refs. 3 and 4 in terms of a general picture, relying solely on Maxwell's equations. This method is not suitable for treating other related results[11,12] in which an isotropic medium is coherently excited near a two-photon resonance, leading to coherent nonlinear optical generation and a reduction of the coherent, two-photon excitation. Such a two-photon excitation is not accompanied by an electric polarization, and a treatment based on linear dielectric response is not appropriate. However, the concept of interference between different pathways of excitation[6,11] is a useful way to understand such results. Finally, Meredith[13] has used a semiclassical description of nonlinear optical generation to treat low-order multiphoton excitation in crystals.

His results also demonstrate that destructive interference between different optical harmonics can lead to a large reduction of the multiphoton excitation.

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[7]Throughout this paper, I will use the convention of only writing the Fourier component at $\exp(-i\omega t)$. The real polarizations and fields are then found by taking the real parts of the complex quantities.

[8]This situation may be viewed as one where $P^{\rm tot}(\omega_G)$ radiates a field $-90°$ out of phase with $E_D(\omega_G)$, with an amplitude such that the resulting wave propagates with the phase velocity $c/[\epsilon_D(\omega_G)]^{1/2}$. For more background, see R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Mass., 1963), Vol. 1, Chap. 31.

[9]In Refs. 3–6, where third-harmonic generation was studied in Xe atomic vapor, $\omega_G = 3\omega$ was resonant with the $5p^6$-$5p^5 6s$ transition at 68 046 cm^{-1}. Since this transition determines $\chi^{\rm lin}$ at 3ω and, along with the nearby transition at 77 186 cm^{-1}, dominates $\chi^{\rm lin}$ at ω, it is straightforward to show that the ratio $|[\epsilon_D(\omega_G) - 1]/[\epsilon_D(\omega_G) - \epsilon(\omega_G)]| = |[\epsilon(\omega) - 1]/[\epsilon(\omega) - \epsilon(3\omega)]| \approx \Gamma/3\omega$, where Γ is an effective linewidth of the resonance due to laser linewidth and pressure, Doppler, and power broadening effects. For a linewidth of $\sim 1\ \mathrm{cm}^{-1}$, this ratio is $\sim 10^{-5}$, showing how dramatically $P^{\rm NLS}$ is renormalized towards zero for a dilute system such as an atomic vapor.

[10]This expression for $E(\omega_G)$ *is* the familiar result for the intensity of em radiation generated at ω_G. For Δk real, $|E(\omega_G)|^2$ is given as Eq. (4-13) on p. 82 of Ref. 2, where the conventional sinusoidal variation with increasing z is explicitly discussed.

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