SECOND HARMONIC GENERATION IN TWO LEVEL SYSTEMS

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(*Received January* 30, 1967; *Resubmitted June* 2, 1967)

ABSTRACT. Interaction of strong electomagnetic field with a two energy level system is considered, with special reference to crystals. Second harmonic generation due to the field dependence of the dipole moment operator is found out. The frequency dependence of the dipole moment expectation value and the field saturation effect have been derived. The detailed relation between the field and the dipole moment, and the d.c. effect have been briefly discussed.

INTRODUCTION

A revival of interest in the study of propagation of electromagnetic waves through crystals, accomodating the nonlinear effects like multiple harmonic generation, has been noticed recently (Briss 1964). This has followed naturally after the observation of second harmonic generation (SHG) in quartz crystal, using a ruby laser source by Franken and others (Franken, et al 1961) and allied effects in other crystals by several other workers (Franken *et al*, 1963). All these effects need highly intense sources (Bonch-Bruevich *et al*, 1965) and for second harmonic generation it is found that the lack of an inversion centre in the crystal is a necessity. These processes can be described by a higher than first order perturbation calculation (Ward 1965), which means that more than two energy levels take part in the interaction. But it is quite possible that second harmonic generation can be observed in systems where only two energy levels are involved in the interaction (Bonch-Bruevich *et al*, 1965). In a previous paper (Mohanty 1967) the author has pointed out two separate conditions which are necessary to generate multiple harmonics of the applied field frequency in a two level system : The presence of a premanent dipole moment in the material system interacting with the field, or, as in the case of crystals, the dependence of the dipole moment operator on the applied field which gives a nonlinear dipole interaction operator in terms of the field. The first condition has already been discussed in the above mentioned paper (Mohanty 1967). The primary aim of this article is to discuss the second condition. Further, considering that only coherent radiation from a laser source is necessary for the process, we will directly find out the expectation value of the dipole moment for a single particle instead of trying to find the probability coefficients and then the transition probability.

DESCRIPTION OF THE MODEL

As our interests primarily lie in the processes where only two energy levels of the material system take part, the technique to be used in this discussion is the geometrical representation of the Schrodinger equation due to Feynman, Vernon and Hellworth (Feynman, *et al.* 1957). This representation involves only two energy levels of the material system, and is quite adequate as a monochromatic incident field is expected to induce a transition primarily between two levels whose transition frequency is nearly equal to the frequency of the field itself. The representation has the added advantage of giving directly the expectation value of the dipole moment operator. The technique is indicated in the previous paper by the author (Mohanty 1967).

The geometrical form of the Schrodinger equation

$$(H_0+V)\psi = i\hbar \frac{d\psi}{dt} \quad \ldots \quad (2.1)$$

for a two level system, where H_0 is the unperturbed hamiltonian and V the interaction operator, is of the form of the equation of motion of a classical gyroscope, as explained by Mohanty (1967).

$$\frac{d\vec{r}}{dt} = \vec{\omega}\times\vec{r} \quad \ldots \quad (2.2)$$

$\vec{r}$ and $\vec{\omega}$ are defined in the previous paper (Mohanty, 1967).

The physical significance of r_i's are immediately found out by taking the expectation values of the dipole moment operator μ and H_0.

$$<\mu> = \int \psi^*\mu\psi dv = \mu_{12}r_1$$

$$<H_0> = \frac{\hbar\omega_{12}}{2} r_3 \quad \ldots \quad (2.3)$$

where μ_{ii} are neglected in comparison with μ_{ij}.

THE DIPOLE INTERACTION

The interaction V, between the field and the material system, is assumed to be of electric dipole type and is expressed by :

$$\vec{V} = -\vec{\mu}.\vec{E} \quad \ldots \quad (3.1)$$

$\vec{\mu}$ being the electric dipole moment operator and $\vec{E}$ is the electric field inducing the transition between the levels. The semiclassical form of V is sufficiently accurate for the present discussion compared to the fully quantum theoretical treatment (Mandel *et al* 1963; Sudarshan 1963). This interaction term is linear in terms of the applied field as long as μ is independent of the field.

But for the intense field which is a necessity in the present case, it is no longer possible to write μ as a single field independent term, as is done in finding out the expectation value of dipole moment which is linear in terms of the applied field. The precise relationship between μ and E is now assumed to be of a tensorial nature, but one can write it in the form (Franken *et al.* 1963);

$$\mu = \mu_0+\mu_1 E+\mu_2 E^2+\ldots \tag{3.2}$$

This schematic relationship, in the form of a power series in E, is sufficient for the present discussion and, as can be seen presently, the full tensorial form in no way changes the result as the same time dependence for all components is assumed in these discussions. The value of successive coefficients μ_i are in rapidly decreasing order (Franken *et al.* 1963) and so only the first two terms are preserved. As mentioned, the use of the first term only gives the linear component of the expectation value of the dipole moment through the linear component of the dipole interaction operator. The second term, however, gives a nonlinear component to the interaction operator, with frequencies 0 and 2ω. This term is expected to contribute to the nonlinear exceptation value of μ.

Writing the interaction term V:

$$V = -\mu_0 E-(\mu_1 E)E$$

$$= \sum_{n=0}^{2} I_n \cos n\omega t = \text{Re.} \sum_{n=0}^{2} I_n e^{-in\omega t} \quad \ldots \tag{3.3}$$

where

$$I_0 = I_2 = \frac{-\mu_1 E_0^2}{2} \;;\quad I_1 = -\mu_0 E_0$$

the nonlinearity of the dipole interaction oprator is now clearly demonstrated.

So,

$$\omega_1 = \sum_n \frac{2(I_n)_{12}}{\hbar} \cos n\omega t$$

$$\omega_2 = \sum_n \frac{2(I_n)_{12}}{\hbar} \sin n\omega t \quad \ldots \tag{3.4}$$

As ω_1 and ω_2 contain sinusoidal terms of three frequencies, 0, ω and 2ω, the values of the $\vec{r}$ components are now expected to contain all these, as well as the higher harmonics of ω. The second harmonic component of $\langle\mu\rangle$ then emerges as the sum of the product of $\mu_1 E$ in eqn. (3.2) and the linear frequency component of r_1, and the product of μ_0 in eqn. (3.2) and the second harmonic component of r_1. One then writes for the second harmonic value of $<\mu>$, using (2.3) and (3.2);

$$<\mu>_{2\omega} = (\mu_{12} r_1)_{2\omega}$$
$$= (\mu_0)_{12}(r_1)_{2\omega}+(\mu_1 E)_{12}(r_1)_\omega \quad \dots \quad (3.5)$$

To solve the eqn. (2.2) one can now subject all the r components to the rotating coordinate transformation given in 1, which gives the changed equation :

$$\frac{dr'}{dt} = \vec{\omega}' \times \vec{r}'$$

with

$$\omega'_1 = (K_1+K_2 \cos \omega t)$$
$$\omega'_2 = 0$$
$$= \omega_{12}-\omega \ ; \qquad K_n = \frac{2(I_n)_{12}}{\hbar}$$

where the V_{11} and V_{22} terms in ω'_3 are neglected in comparision with ω_{12}

The explicit form of the above equation is :

$$\frac{dr'_1}{dt} = -\Delta r'_2$$

$$\frac{dr'_2}{dt} = \Delta r'_1-[K_1+K_2 \cos \omega t]r'_3 \quad \dots \quad (3.7)$$

$$\frac{dr'_3}{dt} = [K_1+K_2 \cos \omega t]r'_2$$

where

$$\Delta = \omega_{12}-\omega.$$

THE VALUE OF $(r_1)_\omega$ AND $(r_1)_{2\omega}$

A solution of the type

$$r'_l = \Sigma\, r_{l,}\, (n)e^{-in\omega t} \quad \dots \quad (4.1)$$

is assumed to solve the set of equations (3.7). $r_{1,\,(0)}$ and $r_{2,(0)}$ are the linear solutions and $r_{1,\,(1)}$ and $r_{2,\,(1)}$ are the second harmonic part.

After performing the necessary differentiation and collecting the coefficients of $e^{-in\omega t}$ one gets :

$$-in\omega r_{1,(n)} = -\Delta r_{2,(n)}$$

$$-in\omega r_{2,(n)} = \Delta r_{1,(n)} - K_1 r_{3,(n)} - \frac{K_1}{2}\left[r_{3,(n-1)} + r_{3,(n+1)}\right]$$

$$-in\omega r_{3,(n)} = K_1 r_{2,(n)} + \frac{K_2}{2}\left[r_{2,(n+1)} + r_{2,(n-1)}\right] \quad \ldots (4.2)$$

One must consider also the symmetry properties of $r_{l,(n)}$'s

$$r_{l,(n)}\left(-\frac{K_2}{2K_1}\right) = (-1)^n \; r_{l,(n)}\left(\frac{K_2}{2K_1}\right) \quad \ldots (4.3)$$

Now putting $\frac{K_2}{2K_1} = Q$; $\frac{\Delta}{K_1} = D$ and $\frac{i\omega}{K_1} = N$;

and expanding $r_{l,(n)}(Q)$ in terms of Q :

$$r_{l,(n)}(Q) = \sum_{j=0}^{\infty} r_{l,(n),j}\, Q^j \quad \ldots (4.4)$$

one sees, using eqn.(4.3), that only even combinations of n and j can exist in the expansion of $r_{l,(n)}(Q)$ in eqn. (3.4).

Using equations (4.2) and (4.4) and collecting the coefficients of Q^j, one gets :

$$nNr_{1,(n),j} = Dr_{2,(n),j}$$

$$-nNr_{2,(n),j} = Dr_{1,(n),j} - r_{3,(n),j} - r_{3,(n+1),(j-1)} - r_{3,(n-1),(j-1)}$$

$$-nNr_{3,(n),j} = r_{2,(n),j} + r_{2,(n+1),(j-1)} + r_{2,(n-1),(j-1)} \quad \ldots (4.5)$$

It is quite easy to seem that for $j = 0$; $r_{l,(n),0}$ is independent of Q(eqn. 4.4) and as this solution may be assumed to be an exact one with only a frequency ω for r_1, and r_2 no higher order solution exists. (Mohanty 1967; for a similar comment, also see Sengupta 1967)
So,

$$r_{l,(n),0} = d_{n0} r_{l,(n),0} \quad \ldots (4.6)$$

Then the zeroeth order ($n = 0$) solution, giving the value of $(r_1)_\omega$ is :

$$r_{2,(0),0} = 0$$

$$r_{1,(0),0} = \frac{1}{D}\, r_{3,(0),0} \quad \ldots (4.7)$$

The first order ($n = 1$) equation is :

$$\begin{aligned} Nr_{1,(1),1} &= Dr_{2,(1),1} \\ -Nr_{2,(1),1} &= Dr_{1,(1),1} - r_{3,(1),1} - r_{3,(0),0} \\ -Nr_{3,(1),1} &= r_{2,(1),1} \end{aligned} \tag{4.8}$$

One then has,

$$\begin{aligned} r_{1,(0),0} &= \frac{K_1}{\ldots} r_{3,(0),0} \\ r_{1,(1),1} &= \frac{\Delta K_1}{\Delta^2 - \omega^2 + K_1^2} r_{3,(0),0} \\ r_{2,(1),1} &= \frac{i\omega K_1}{\Delta^2 - \omega^2 + K_1^2} r_{3,(0),0} \end{aligned} \tag{4.9}$$

Effecting the inverse transformation given in (Mohanty 1967) and collecting the relevent terms :

$$\begin{aligned} r_1(\omega) &= \frac{K_1}{\omega_{12} - \omega} r_{3,(0),0} \cos \omega t \\ r_1(0) &= \frac{1}{4} \frac{K_2(\omega_{12} - 2\omega)}{\omega_{12}(\omega_{12} - 2\omega) + K^2} r_{3,(0),0} \\ r_1(2\omega) &= \frac{1}{4} \frac{K_2 \omega_{12}}{\omega_{12}(\omega_{12} - 2\omega) + K_1^2} r_{3,(0),0} \cos 2\omega t \end{aligned} \tag{4.10}$$

From these values, making use of eqn. (2.3) we have,

$$<\mu>_{2\omega} = (2\hbar)^{-1} r_{3,(0),0} \left[\frac{(\mu_0)_{12}(\mu_0 E_0^2)_{12}}{2(\omega_{12} - 2\omega) + 2K_1^2/\omega_{12}} + \frac{2(\mu_1 E_0)_{12}(\mu_0 E_0)_{12}}{(\omega_{12} - \omega)} \right] \cos 2\omega t \quad \ldots \tag{4.11a}$$

$$<\mu>_0 = (2\hbar)^{-1} r_{3,(0),0} \left[\frac{2(\mu_1 E_0)_{12} (\mu_0 E_0)_{12}}{(\omega_{12} - \omega)} + \frac{1}{2} \frac{(\mu_0)_{12}(\mu_1 E_0^2)_{12}(\omega_{12} - 2\omega)}{(\omega_{12} - 2\omega)\omega_{12} + K_1^2} \right] \tag{4.11b}$$

DISCUSSION

We shall now discuss the exact tensorial nature of μ . The schematic dependence of polarisation P(dipole moment per unit volume) and the field E is written down as (Bonch-Bruevich *et al.* 1965);

$$P = \chi_0 E + \chi E^2 + \ldots \quad \ldots \tag{5.1}$$

The process of second harmonic generation is described by χ, and it is evident that this is related to $<\mu>_{0,2\omega}$ of the eqn. (4.11). For the generation of second harmonic an essential condition is the lack of a symmetry centre in the crystal, otherwise a strong, static electric field must be applied to enhance the nonlinearity of the relation between the crystal polarisation and the applied field. In general, for such a case the quadratic part of P is written down as

$$P_i^{(2)} = \Sigma\ \Sigma \chi_{ijk} E_j E_k \tag{5.2}$$

Consideration of the fact that the order of writing down the fields E_j and E_k is is immaterial and that this tensor is formally similar to the piezo-electric tensor (Franken *et al.* 1961) enables us to write down a contracted form by replacing the suffixes i, j by only one suffix m. A further symmetry restriction proposed by Kleinman (1962) allows the inter-change of i and j, which has the advantage of reducing the number of independent tensor elements. χ is a 3×6 tensor, and particularly, for quartz,

$$P^{(2)} = \begin{vmatrix} \chi_{11} & -\chi_{11} & 0 & \chi_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\chi_{14} & -\chi_{14} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix} \begin{matrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{matrix} \quad \ldots \tag{5.3}$$

By suitable experimental arrangements the contribution from some elements can be reduced and one can check the additional symmetry requirements (Miller 1963). Under this condition eqn. (5.3) gives :

$$P^{(2)} = \hat{i}\chi_{11}E_x^2 - \hat{j}2\chi_{14}E_xE_z \tag{5.4}$$

A comparison of the contributions from χ_{11} and χ_{14} shows that $\chi_{11} >> \chi_{14}$ for a ruby laser. This demonstrates the possibility of reducing the number of elements of the tensor by suitabe arrangements.

Finally a few words about the generation of a frequency independent part of $<\mu>$, otherwise known as the d.c. effect are in order. An inspection of the value of $<\mu>_0$ in eqn. (4.11b) shows the inherent difficulties in the experimental detection of this effect. At $\omega_{12} = \omega$, as the fundamental harmonic part of $<\mu> = <\mu>_\omega$ predominates; and also at $\omega_{12} = 2\omega$, as there is negligible power transfer at or near this frequency in the case of $<\mu>_0$, it is a difficult effect to detect. This may explain the inconveniences originally encountered in the observation of this effect.

ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. H. G. Venkates for his guidance and Prof. H. N. Bose for his kind encouragement in carrying out this piece of research. The author is also indebted to Prof. N. D. Sengupta for some stimulating discussions.

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