Nonlinear Optical Frequency Polarization in a Dielectric

ERIC ADLER
IBM Watson Laboratory and Physics Department, Columbia University, New York, New York
(Received 25 July 1963)

A perturbation calculation of optical frequency polarization quadratic in the Maxwell field is made for a dielectric in which the electrons are localized on units of the crystal. The result is expressed in a power series in $K\langle r\rangle\sim10^{-3}$ where $\langle r\rangle$ is the size of the unit and K is the wave number of the field. The term of zeroth order is the electric-dipole term which vanishes in a crystal with a center of symmetry. The term first order in $K\langle r\rangle$ is separated into electric-quadrupole and magnetic-dipole contributions by introducing a special gauge for the electromagnetic potentials. Higher power terms are neglected.

1. INTRODUCTION

WHEN two coherent laser beams pass through a dielectric, the emerging light may contain radiation at the sum and difference frequencies of the incident beams[1] in addition to harmonics of the incident frequencies.[2] Static electric polarization of a dielectric by a laser beam has also been observed.[3] These effects occur because induced polarization $\mathbf{P}$ in the dielectric is nonlinear in the applied fields $\mathbf{E}$.

Polarization being a polar vector, an expression for the polarization quadratic in the applied fields, $\mathbf{P}^{\mathrm{II}}$, can be constructed from products of three polar vectors, and from suitable products of axial and polar vectors. When the crystal lacks inversion symmetry, quartz and K.D.P., for example, we may write $P_\alpha{}^{\mathrm{II}}=\rho_{\alpha\beta\gamma}E_\beta E_\gamma$.[4] We have two polar vectors supplied by the electric field and the third by a vector direction in the crystal. Most authors have considered only this type of quadratic polarization.

Polarization quadratic in the fields has also been observed in calcite, whose crystal structure has a center of symmetry.[4] We shall show that in the absence of a vector defined in the crystal we can expect a quadratic polarization given by the phenomenological relation

$$P_\alpha{}^{\mathrm{II}}=G_{\alpha\beta\gamma}B_\beta E_\gamma+D_{\alpha\beta\gamma\delta}E_\beta(\partial/\partial r_\gamma)E_\delta. \quad (1.1)$$

The first term in (1.1) is a product of a polar vector $\mathbf{E}$ and an axial vector, the magnetic field $\mathbf{B}$. The second term is a product of three polar vectors; $\partial/\partial\mathbf{r}$, operating on $\mathbf{E}$, is equivalent to the wave vector of the incident light. G, D, and ρ are functions of the frequencies of the incident beams.

The following rough consideration leads to (1.1). In all polarizable media, there is a force density on the particles of the medium given classically by

$$\mathbf{F}^{\mathrm{II}}=-\tfrac{1}{2}\nabla(\mathbf{E}\cdot\mathbf{P}^{\mathrm{I}})-(1/c)\mathbf{B}\times\partial\mathbf{P}^{\mathrm{I}}/\partial t.$$

The quadratic polarization may be regarded heuristically as the linear polarization induced by $\mathbf{F}$. If the linear polarizability is $\boldsymbol{\alpha}$, we may write $P_\alpha=(nq)^{-1}\alpha_{\alpha\beta}F_\beta$ where n is the effective number of particles per unit volume which contribute to the polarizability $\boldsymbol{\alpha}$, q their charge, and $\mathbf{F}$ the force density. Since $P_\alpha{}^{\mathrm{I}}=\alpha_{\alpha\beta}E_\beta$, we get

$$P_\alpha{}^{\mathrm{II}}=(nq)^{-1}[\alpha_{\alpha\beta}\alpha_{\gamma\delta}E_\delta(\partial/\partial r_\beta)E_\gamma+\alpha_{\alpha\beta}\alpha_{\gamma\lambda}\epsilon_{\beta\gamma\delta}B_\delta(\partial/\partial t)E_\lambda], \quad (1.2)$$

which is the form (1.1). The frequency dependence of α should not be forgotten.

From Maxwell's equations, we see that the first and second terms on the right of (1.2) are the same order of magnitude. Using the above model for fused $PbSiO_3$, which has a refractive index of 1.9 at a wavelength of 6×10^{-5} cm, taking $n=2\times10^{23}$ cm^{-3}, we find

$$|P^{\mathrm{II}}/P^{\mathrm{I}}|\sim E/(2\times10^{12}\ \mathrm{V\ cm^{-1}}).$$

For a static magnetic field $\mathbf{B}$, the second term is the polarization component that causes the Faraday rotation.[5] Thus, we can estimate $|P^{\mathrm{II}}/P^{\mathrm{I}}|$ for materials with inversion symmetry from the experimentally determined Verdet constants. In fused $PbSiO_3$, the Verdet constant is 7.9×10^{-2} min/(G cm), and we calculate from this $|P^{\mathrm{II}}/P^{\mathrm{I}}|\sim E/(2\times10^{12}\ \mathrm{V\ cm^{-1}})$ in agreement with the calculation based on (1.2).

Expressions for these polarization effects are calculated in Sec. 2 using a crude classical model of a dielectric. More rigorously, in Sec. 3 we begin a quantum-mechanical calculation of the relation between the Fourier components $\mathbf{E}^{\mathbf{K}}{}_\omega$, $\mathbf{B}^{\mathbf{K}}{}_\omega$ of the fields and $\mathbf{J}^{\mathbf{K}_1+\mathbf{K}_2}{}_{\omega_1+\omega_2}$ the expectation of the electron current density quadratic in the fields. Instead of using Bloch functions as our basis states, we shall make the calculation in terms of electron wave functions localized on units of the crystal. We seek the first two terms in the expansion of $\mathbf{J}^{\mathbf{K}_1+\mathbf{K}_2}{}_{\omega_1+\omega_2}$ in a power series in K_1 and K_2; i.e., the terms of zeroth and first degree in the K's. The ratio of the latter to the former is in general of order $K\langle r\rangle$, where $\langle r\rangle$ is the order of the dimensions of our unit, and we shall be concerned with conditions where $K\langle r\rangle\approx10^{-3}$. The terms of zeroth degree in the K's vanish if the medium has inversion symmetry. Intro-

[1] M. Bass, P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **8**, 18 (1962).
[2] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).
[3] M. Bass, P. A. Franken, J. F. Ward, and G. Weinreich, Phys. Rev. Letters **9**, 446 (1962).
[4] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Letters **8**, 404 (1962).
[5] R. Serber, Phys. Rev. **41**, 489 (1932).

duction of a suitable gauge for the electromagnetic potentials enables us to put the perturbing part of the Hamiltonian in a form linear in the fields, to first power in $K\langle r\rangle$. In this gauge, the Fourier component of the current-density operator becomes independent of the fields to first order in $K\langle r\rangle$. $\mathbf{J}^{\mathbf{K}_1+\mathbf{K}_2}{}_{\omega_1+\omega_2}$ can then be calculated wholly as a second-order perturbation.

Armstrong *et al.*[6] and Franken and Ward[7] have treated many aspects of nonlinear optical phenomena and made quantum-mechanical calculations of the second-order polarization. Both of these papers and the other theoretical papers on the subject do the theory applicable only in the absence of inversion symmetry. For this case, the results of this paper are in agreement with the literature.

2. CLASSICAL MODELS

A first view of the microscopic basis of the foregoing phenomena may be obtained by representing the dielectric as a lattice of charged harmonic oscillators with appropriate refinements. For the case where the lattice lacks a center of inversion, one makes the oscillator anharmonic by the addition of a force quadratic in r, the displacement of the charge[8] (though quantum mechanically such a system is bound only metastably). The equation of motion of the anharmonic oscillator may be written

$$m(d^2r_\alpha/dt^2+\omega_0^2r_\alpha)+\chi_{\alpha\beta\gamma}r_\beta r_\gamma=qE_\alpha(t)\,, \qquad (2.1)$$

on neglecting local-field corrections, Lorentz forces, and space variations of the fields over molecular distances. We let

$$E_\alpha(t)=E_{\alpha,\omega_1}\exp(i\omega_1 t)+E_{\alpha,\omega_2}\exp(i\omega_2 t)+\text{c.c.}\,, \qquad (2.2)$$

and similarly,

$$r_\alpha=r_{\alpha,\omega_1}e^{i\omega_1 t}+r_{\alpha,\omega_2}e^{i\omega_2 t}+r_{\alpha,\omega_1+\omega_2}e^{i(\omega_1+\omega_2)t}+\text{etc.}\\ +\text{c.c.} \qquad (2.3)$$

Fourier analyzing (2.1), to first order in $E_{\alpha,\omega}$,

$$r_{\alpha,}{}^{\mathrm{I}}{}_\omega=qm^{-1}E_{\alpha,\omega}/(\omega_0^2-\omega^2)\,. \qquad (2.4)$$

Using this solution, we find, for the second-order term

$$P_{\alpha,}{}^{\mathrm{II}}{}_{\omega_1+\omega_2}=nqr_{\alpha,}{}^{\mathrm{II}}{}_{\omega_1+\omega_2}\\ =\frac{(q/m)^3N\chi_{\alpha\beta\gamma}(E_{\beta,\omega_1}E_{\gamma,\omega_2}+E_{\beta,\omega_2}E_{\gamma,\omega_1})}{(\omega_0^2-\omega_1^2)(\omega_0^2-\omega_2^2)(\omega_0^2-(\omega_1+\omega_2)^2)}\,. \qquad (2.5)$$

The same result may be derived quantum mechanically, treating (2.1) as the Heisenberg equation. However, in contrast with the situation for linear polarization, an arbitrary potential does *not* give this dispersion form, i.e., for a general system $\rho_{\alpha\beta\gamma}{}^{(\omega_1,\omega_2)}$ is not a sum of terms like (2.4) with different ω_0 weighted with different oscillator strengths.

In the limit $\omega\to 0$, $|P^{\mathrm{II}}{}_{2\omega}/P^{\mathrm{I}}{}_\omega|=E_\omega/E_0$, where $E_0=(m\omega_0^2)^2/\chi q$. A lower limit for E_0, for highly asymmetric molecules is about 10^8 V/cm, the magnitude of atomic fields.

When inversion symmetry is present in the crystal, there is no anharmonic force term. The Lorentz force and the space variation of the electric field now become important in the equation of motion.

$$m(d^2\mathbf{r}/dt^2+\omega_0^2\mathbf{r})=q[\mathbf{E}(\mathbf{r},t)+(1/c)(d\mathbf{r}/dt)\times\mathbf{B}]\,. \qquad (2.6)$$

Let

$$\mathbf{E}=\mathbf{E}_{\omega_1}\exp[i(\omega_1 t-\mathbf{K}_1\cdot\mathbf{r})]\\ +\mathbf{E}_{\omega_2}\exp[i(\omega_2 t-\mathbf{K}_2\cdot\mathbf{r})]+\text{c.c.}\\ \mathbf{B}=\mathbf{B}_{\omega_1}\exp[i(\omega_1 t-\mathbf{K}_1\cdot\mathbf{r})]\\ +\mathbf{B}_{\omega_2}\exp[i(\omega_2 t-\mathbf{K}_2\cdot\mathbf{r})]+\text{c.c.} \qquad (2.7)$$

We expand the right-hand side of (2.7) in powers of $\mathbf{K}\cdot\mathbf{r}$ and, substituting the resulting series in (2.6), we take the Fourier transforms of this equation. To first order in $\mathbf{K}\cdot\mathbf{r}$ ($K\cong\omega/c$),

$$\mathbf{r}_{\omega_1+\omega_2}=\frac{(q/m)^2(-\mathbf{E}_{\omega_1}i\mathbf{K}_1\cdot\mathbf{E}_{\omega_2}+i(\omega_2/c)\mathbf{E}_{\omega_2}\times\mathbf{B}_{\omega_1})}{(\omega_0^2-(\omega_1+\omega_2)^2)(\omega_0^2-\omega_2^2)}\\ +\text{a term interchanging the roles of 1 and 2.} \qquad (2.8)$$

The Heisenberg equation of motion for $\mathbf{r}$ has a solution, for the expectation of $\mathbf{r}_{\omega_1+\omega_2}$, identical with (2.8) upon making the same approximations made above.

The expression for $P^{\mathrm{II}}{}_{\omega_1+\omega_2}$ resulting from (2.8) is identical in form with (1.2), since $\alpha(\omega)=(q^2/m)n\times(\omega_0^2-\omega^2)^{-1}$; $\nabla\mathbf{E}_\omega=-i\mathbf{K}\mathbf{E}_\omega$; $(\partial/\partial t)\mathbf{E}_\omega=i\omega\mathbf{E}_\omega$.

$$\mathbf{P}^{\mathrm{II}}{}_{\omega_1+\omega_2}=\alpha(\omega_2)\alpha(\omega_1)(qn)^{-1}\\ \times(-i\mathbf{K}\cdot\mathbf{E}_{\omega_2}\mathbf{E}_{\omega_1}+i(\omega_2/c)\mathbf{E}_{\omega_2}\times\mathbf{B}_{\omega_1})\\ +\text{a term interchanging the roles of 1 and 2.}$$

In the following two sections, the dielectric is still represented as a lattice of identical, independent units; but no assumption is made about the character of these units, and the quadratic polarization due to such a lattice is calculated in an essentially exact way.

3. LOCALIZED CURRENT DENSITY AND HAMILTONIAN

We want to calculate the portion of the Fourier component of the electron current density which is quadratic in the exciting fields. The current-density operator, in the two component Pauli spin space, at the point $\mathbf{r}$ is[9]

$$\mathbf{J}(\mathbf{r})=\textstyle\sum_i(\{(q/m)\{\boldsymbol{\pi}_i,\delta(\mathbf{r}-\mathbf{r}_i)\}+c\mu\nabla\times\{\boldsymbol{\sigma}_i,\delta(\mathbf{r}-\mathbf{r}_i)\}\\ +(\mu/m)(d/dt)(\{\boldsymbol{\pi}_i,\delta(\mathbf{r}-\mathbf{r}_i)\}\times\boldsymbol{\sigma}_i))\,, \qquad (3.1)$$

[6] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).
[7] P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).
[8] Benjamin Lax, J. O. Mavroides, and D. F. Edwards, Phys. Rev. Letters **8**, 166 (1962).
[9] I. A. Frenkel, *Wave Mechanics; Advanced General Theory* (Dover Publications Inc., New York, 1950), p. 322.

where

$$\boldsymbol{\pi}_i=\mathbf{p}_i-(q/c)\mathbf{A}(\mathbf{r}_i);\quad \{A,B\}=\tfrac{1}{2}(AB+BA).$$

$\mathbf{A}(\mathbf{r})$ is the vector potential; $\mathbf{p}_i$ is the momentum operator of the ith electron. The sum is over all N electrons. The expectation of the first term in the bracket on the right of (3.1) is simply the charge density times the velocity of electron i. The second term is c times the curl of the density of intrinsic electron magnetic moments $\mu\boldsymbol{\sigma}_i$. The last term is the rate of change of the electric-dipole moments resulting from the motion of magnetic dipoles.

Then a Fourier component of the current density is the expectation of the operator

$$\begin{aligned}\mathbf{J}^{\mathbf{K}}&=\int\mathbf{J}(\mathbf{r})\exp(i\mathbf{K}\cdot\mathbf{r})d\mathbf{r}\\&=\sum_i[(q/m)\{\boldsymbol{\pi}_i,\exp(i\mathbf{K}\cdot\mathbf{r}_i)\}\\&\quad-c\mu i(\mathbf{K}\times\boldsymbol{\sigma}_i)\exp(i\mathbf{K}\cdot\mathbf{r}_i)\\&\quad+(\mu/mc)(d/dt)(\{\boldsymbol{\pi}_i,\exp(i\mathbf{K}\cdot\mathbf{r}_i)\}\times\boldsymbol{\sigma}_i)].\end{aligned}\tag{3.2}$$

Neglecting spin-orbit coupling, the Hamiltonian for the electrons is $H=H_0+H'$, where

$$H_0=\sum_i\mathbf{p}_i^2/2m+V(\mathbf{r}_1,\cdots\mathbf{r}_i,\cdots\mathbf{r}_n),\tag{3.3a}$$

$$\begin{aligned}H'=\sum_i[&-(q/2mc)\{p_{i,\alpha},A_\alpha(\mathbf{r})_i\}-\mu\mathbf{B}(\mathbf{r}_i)\cdot\boldsymbol{\sigma}_i\\&+q\phi(\mathbf{r}_i)+(q^2/2mc^2)A^2(\mathbf{r}_i)].\end{aligned}\tag{3.3b}$$

The right-hand side of (3.2) contains some terms linear in the fields, whose expectation to first order in H' is at least quadratic in the fields. Furthermore, the last term in (3.3b) is already quadratic in the fields. We must therefore treat some combinations of terms in H' and $\mathbf{J}^{\mathbf{K}}$ by first-order perturbation theory, and some by second-order perturbation theory. The results obtained in this manner are not easy to interpret if the usual transverse gauge is used for the electromagnetic potentials.

If we use Bloch functions as our unperturbed wave functions, our choice of gauge is limited to $\mathbf{A}(\mathbf{r})$, $\phi(\mathbf{r})$ periodic in $\mathbf{r}$; otherwise, applying $\mathbf{A}(\mathbf{r})$ or $\phi(\mathbf{r})$ to a state will take us outside the domain of periodic functions. In this paper, instead of using Bloch functions we shall suppose that the eigenfunctions of the unperturbed Hamiltonian localize each electron on a unit (atom or molecule) of dimensions $\langle r\rangle\ll 1/K$. We then calculate $\mathbf{J}(\mathbf{R})^{\mathbf{K}}$, the contribution to the Fourier component of the current-density operator from the unit whose center is located at $\mathbf{R}$, and then sum over all units of the system

$$\mathbf{J}^{\mathbf{K}}=\sum_{\mathbf{R}}\mathbf{J}(\mathbf{R})^{\mathbf{K}}.\tag{3.4a}$$

where

$$\begin{aligned}\mathbf{J}(\mathbf{R})^{\mathbf{K}}=\exp(i\mathbf{K}\cdot\mathbf{R})\sum_j[&(q/m)\{\boldsymbol{\pi}_j,\exp(i\mathbf{K}\cdot\mathbf{r}_j')\}\\&-c\mu i\mathbf{K}\times\boldsymbol{\sigma}_j\exp(i\mathbf{K}\cdot\mathbf{r}_j')\\&+(\mu/mc)(d/dt)\{\boldsymbol{\pi}_j,\exp(i\mathbf{K}\cdot\mathbf{r}_j')\}\times\boldsymbol{\sigma}_j].\end{aligned}\tag{3.4b}$$

The summation on j is over all electrons on the unit located at $\mathbf{R}$, and $\mathbf{r}_j'=\mathbf{r}_j-\mathbf{R}$.

We can expand the $\exp(i\mathbf{K}\cdot\mathbf{r}')$ in (3.4b) in powers of $\mathbf{K}\cdot\mathbf{r}'$ and consider terms up to first power in $(\mathbf{K}\cdot\mathbf{r}')$. (We will hereafter drop the primes on $\mathbf{r}_j'$.) This approximation is justified for our model in which the electrons are localized. We get

$$\begin{aligned}\mathbf{J}(\mathbf{R})^{\mathbf{K}}=\exp(i\mathbf{K}\cdot\mathbf{R})\sum_j\Big(&q\frac{d}{dt}\mathbf{r}_j+\frac{i}{2}q\frac{d}{dt}(\mathbf{K}\cdot\mathbf{r}_j\mathbf{r}_j)\\&-(q/2m)i\mathbf{K}\times(\mathbf{L}_j+\hbar\boldsymbol{\sigma}_j)\\&+(q/2mc)i\mathbf{K}\times(\mathbf{r}_j\times\mathbf{A}(\mathbf{r}_j))\\&+(\hbar q/2m)(\mathbf{K}\times\boldsymbol{\sigma}_j)(\mathbf{K}\cdot\mathbf{r}_j)\\&+(\hbar q/2mc^2)\frac{d}{dt}\left(\left(\frac{d}{dt}\mathbf{r}_j\right)\times\boldsymbol{\sigma}_j+\left(\frac{i}{2}\frac{d}{dt}(\mathbf{K}\cdot\mathbf{r}_j\mathbf{r}_j)\right)\times\boldsymbol{\sigma}_j\right)\\&-i(\hbar q/4mc^2)\frac{d}{dt}((\mathbf{K}\times(\mathbf{L}_j-\mathbf{r}_j\times\mathbf{A}(\mathbf{r}_j))\times\boldsymbol{\sigma}_j)\Big),\end{aligned}\tag{3.5}$$

where $\mathbf{L}_j=\mathbf{r}_j\times\mathbf{p}_j$ is the angular momentum about $\mathbf{R}$. With the gauge described in the Appendix, in which the potentials are explicit functions of the $\mathbf{r}'$ and are distinct for each $\mathbf{R}$, it is shown there that only the first three terms on the right-hand side of (3.5) contribute to the quadratic part of $\mathbf{J}(\mathbf{R})^{\mathbf{K}}$ up to first order in $K\langle r\rangle$ or $\langle p\rangle/mc$. At optical frequencies, $K\sim 10^{-5}$ cm^{-1} and these are of the same order of magnitude: $\langle r\rangle\sim 10^{-8}$ cm, $K\langle r\rangle\sim 10^{-3}$, $\langle p\rangle\sim\hbar/\langle r\rangle$, $\langle p\rangle/mc\sim 10^{-3}$. Consequently, the operator $\mathbf{J}(\mathbf{R})^{\mathbf{K}}$ can be taken independent of the fields.

$$\mathbf{J}(\mathbf{R})^{\mathbf{K}}=\exp(i\mathbf{K}\cdot\mathbf{R})(d\mathbf{X}/dt+i\mathbf{K}\cdot d\mathbf{Q}/dt-ic\mathbf{K}\times\mathbf{M}).\tag{3.6}$$

The operator $\mathbf{X}=\sum_j q\mathbf{r}_j$ is the total electric-dipole moment of the unit; $Q=\frac{1}{2}\sum_j q\mathbf{r}_j\mathbf{r}_j$ is the total electric-quadrupole moment and

$$\mathbf{M}=(q/2mc)\times\sum_j(\mathbf{r}_j\times\mathbf{p}_j+\hbar\boldsymbol{\sigma}_j),$$

the total magnetic moment. The sum is over all electrons on the unit located at $\mathbf{R}$.

It is shown in the Appendix that the portion of H' acting on the electrons at $\mathbf{R}$ is linear in the fields to order $K\langle r\rangle$ or $\langle p\rangle/mc$, if the gauge introduced there is used.

$$\begin{aligned}&H'=\sum_{\mathbf{R}}H'(\mathbf{R}),\\&H'(\mathbf{R})=\sum_a[\{\mathbf{X}\cdot\mathbf{E}_a+i\mathbf{K}_a\cdot\mathbf{Q}\cdot\mathbf{E}_a-\mathbf{B}_a\cdot\mathbf{M}\}\\&\qquad\times\exp i(\theta_a-\mathbf{K}_a\cdot\mathbf{R})]e^{i\omega_a t}+O(\langle Kr\rangle^2)\\&\qquad\qquad+\text{Hermitian conjugate},\end{aligned}\tag{3.7}$$

where the electromagnetic field is a sum of traveling waves of wave vector $\mathbf{K}_a$, frequency ω_a. Therefore, the contribution to $\mathbf{J}^{\mathbf{K}}$ quadratic in the Maxwell field of each unit may be calculated up to first order in $\mathbf{K}$ solely by second-order perturbation theory.

TABLE I. $J_\alpha(\mathbf{R})^{\mathbf{K}_1+\mathbf{K}_2}=\exp i[(\omega_1+\omega_2)t+\theta_1+\theta_2]$ times the sum of the elements in the left-hand column. The numbers 1 and 2 under the heading "Perturbations" refer to the frequencies of the perturbing fields.

Contribution to $J_\alpha(\mathbf{R})^{\mathbf{K}_1+\mathbf{K}_2}$	Perturbed quantity	Perturbations 1	2
(1) $E_{1\gamma}E_{2\delta}\rho_{\alpha\gamma\delta}{}^{(\omega_1,\omega_2)}$	a	d	d
(2) $B_{1\gamma}B_{2\lambda}\Gamma_{\alpha\gamma\lambda}{}^{(\omega_1,\omega_2)}$	a	f	d
(3) $E_{1\lambda}B_{2\gamma}\Gamma_{\alpha\gamma\lambda}{}^{(\omega_2,\omega_1)}$	a	d	f
(4) $i(K_{1\sigma}+K_{2\sigma})E_{2\gamma}E_{1\delta}\Sigma_{\alpha\sigma\gamma\delta}{}^{(\omega_1,\omega_2)}$	c	d	d
(5) $iK_{2\delta}E_{2\gamma}E_{1\lambda}\Delta_{\alpha\gamma\delta\lambda}{}^{(\omega_2,\omega_1)}$	a	d	e
(6) $iK_{1\delta}E_{1\gamma}E_{2\lambda}\Delta_{\alpha\gamma\delta\lambda}{}^{(\omega_1,\omega_2)}$	a	e	d
(7) $i(K_{1\beta}+K_{2\beta})E_{1\gamma}E_{2\lambda}\Lambda_{\alpha\beta\gamma\delta}{}^{(\omega_1,\omega_2)}$	b	d	d

$a=d\mathbf{X}/dt$ $\quad d=-\mathbf{E}\cdot\mathbf{X}$

$b=i\mathbf{K}\cdot d\mathbf{Q}/dt$ $\quad e=i\mathbf{K}\cdot\mathbf{E}\cdot\mathbf{Q}$

$c=ic\mathbf{K}\times\mathbf{M}$ $\quad f=-\mathbf{B}\cdot\mathbf{M}$

For the part of the perturbing field which is a sum of two traveling waves, with wave vectors $\mathbf{K}_1$, $\mathbf{K}_2$ and frequencies ω_1, ω_2, the corresponding part of $\langle\mathbf{J}(\mathbf{R})^{\mathbf{K}}\rangle$ that is bilinear in the fields will have the form

$$\langle\mathbf{J}(\mathbf{R})^{\mathbf{K}}\rangle_{\omega_1+\omega_2}=\mathbf{C}^{\mathbf{K}}{}_{\omega_1+\omega_2}\exp i[(\mathbf{K}-\mathbf{K}_1-\mathbf{K}_2)\cdot\mathbf{R}+(\omega_1+\omega_2)t+\theta_1+\theta_2],$$

where $C^{\mathbf{K}}{}_{\omega_1+\omega_2}$ is a constant independent of $\mathbf{R}$. After performing the sum indicated in (3.4a) we find $\langle\mathbf{J}^{\mathbf{K}}\rangle_{\omega_1+\omega_2}=0$, unless $\mathbf{K}=\mathbf{K}_1+\mathbf{K}_2$ when $\langle\mathbf{J}^{\mathbf{K}_1+\mathbf{K}_2}\rangle_{\omega_1+\omega_2}=N\mathbf{C}^{\mathbf{K}_1+\mathbf{K}_2}{}_{\omega_1+\omega_2}$ where, N is the total number of units. Similarly for $\omega_1-\omega_2$, $\mathbf{K}_1-\mathbf{K}_2$, etc.

4. CALCULATION OF THE POLARIZATION CURRENT

We may write the linearized perturbation as

$$H'(\mathbf{R})=\sum a(H_a'\exp(i\omega_a t)+H_a'^{\dagger}\exp(-i\omega_a t)), \quad (4.1)$$

and assume that the fields causing the perturbation are turned on exponentially slowly at $t=-\infty$, when the system is in the eigenstate of H_0, $|0\rangle$.

The expectation of an operator G may be expanded in powers of the perturbation at time t:

$$\langle G\rangle_{00}=G_0{}^0+G_0{}^{(1)}+G_0{}^{(2)}\cdots, \quad (4.2)$$

where $G_0{}^{(0)}=\langle 0|G|0\rangle$.

The superscripts stand for the powers of H' which appear in each term. Let $|n\rangle$ be the eigenstate of H_0 with energy $\hbar\omega_n$, and let $\omega_{mn}\neq\omega_a$, $\omega_a+\omega_b$. If the operator G is time independent in the Schrödinger picture, and independent of the fields responsible for the perturbation, then

$$G_0{}^{(1)}=\sum_a\left[\sum{}'_n\left\{\frac{\langle 0|G|n\rangle\langle n|H'_a|0\rangle}{\hbar(\omega_{n0}+\omega_a)}+\frac{\langle n|H'_a{}^{\dagger}|0\rangle^*\langle n|G|0\rangle}{\hbar(\omega_{n0}-\omega_a)}\right\}\exp(i\omega t)+\text{c.c.}\right]. \quad (4.3)$$

The prime over the summation means $n\neq 0$ throughout. The expression in the square bracket of (4.3) is the linear response of $\langle G\rangle$ to the perturbation at frequency ω_a.

Let two distinct perturbations of frequency ω_1 and ω_2 be present. The portion of $G_0{}^{(2)}$ which oscillates at frequency $\omega_1+\omega_2$ is then given by

$$G^{(2)}{}_{0,\omega_1+\omega_2}=G^{(2)}{}_{0,12}+G^{(2)}{}_{0,21},$$

where

$$G^{(2)}{}_{0,ab}=(1/\hbar^2)\sum_l\sum_n\left\{\frac{\langle n|H'_a{}^{\dagger}|0\rangle^*\langle n|G|l\rangle\langle l|H'_b|0\rangle}{(\omega_{n0}-\omega_a)(\omega_{l0}+\omega_b)}+\frac{\langle n|H'_a|l\rangle^*\langle l|H'_b{}^{\dagger}|0\rangle\langle n|G|0\rangle}{(\omega_{l0}-\omega_b)(\omega_{n0}-\omega_a-\omega_b)}+\frac{\langle 0|G|n\rangle\langle n|H'_a|l\rangle\langle l|H'_b|0\rangle}{(\omega_{n0}+\omega_a+\omega_b)(\omega_{l0}+\omega_b)}\right\}\times\exp(i(\omega_a+\omega_b)t). \quad (4.4)$$

H'_a is simply the contents of the square bracket of (3.7). For G we take the first three terms on the right-hand side of (3.5),

$$\mathbf{J}(\mathbf{R})^{\mathbf{K}}=\left(\frac{d}{dt}\mathbf{X}+i\frac{d}{dt}\mathbf{K}\cdot\mathbf{Q}-ic\mathbf{K}\times\mathbf{M}\right)\exp(i\mathbf{K}\cdot\mathbf{R}). \quad (3.6)$$

Table I collects the terms of interest contributing to $\langle\mathbf{J}^{\mathbf{K}}\rangle^{(2)}{}_{\omega_1+\omega_2}$. Any combination of terms from H' and $\mathbf{J}(\mathbf{R})^{\mathbf{K}}$ missing from the table is down by a further factor of $K\langle r\rangle$ or $\langle p\rangle/mc$. In all the expressions which follow, calculations have been made using real wave functions for the eigenstates $|n\rangle$ (i.e., we have excluded spin-orbit coupling) and on the assumption that

$$\langle 0|\textstyle\sum_j\boldsymbol{\sigma}_j|0\rangle=0. \quad (4.5)$$

The first term in the left-hand column of Table I is the standard electric-dipole term of zeroth order in $K\langle r\rangle$. It is the only one which vanishes with inversion symmetry. It corresponds to the polarization calculated with the anharmonic oscillator model in Sec. 2, but the result does not necessarily reduce to a sum of terms like (2.4). We find

$$\rho_{\alpha\gamma\delta}{}^{(\omega_1,\omega_2)}=\left(\frac{2i}{\hbar^2}\right)(\omega_1+\omega_2)\sum_l\sum_n\left[\frac{\langle 0|X_\delta|n\rangle\langle n|X_\alpha|l\rangle\langle l|X_\gamma|0\rangle}{(\omega_{n0}{}^2-\omega_2{}^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{l0}\omega_{n0}-\omega_1\omega_2)+\frac{\langle 0|X_\alpha|n\rangle\langle n|X_\delta|l\rangle\langle l|X_\gamma|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{n0}\omega_{l0}+\omega_1(\omega_1+\omega_2))+\frac{\langle 0|x_\alpha|n\rangle\langle n|X_\gamma|l\rangle\langle l|X_\delta|0\rangle(\omega_{n0}\omega_{l0}+\omega_2(\omega_1+\omega_2))}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_2{}^2)}\right]. \quad (4.6)$$

The following terms are the significant ones for a system having a center of symmetry. We have

$$\Gamma_{\alpha\gamma\lambda}{}^{(\omega_2,\omega_1)}=\left(\frac{2i}{\hbar^2}\right)(\omega_1+\omega_2)\sum_l\sum_n\left[\frac{\langle 0|X_\lambda|n\rangle\langle n|X_\alpha|l\rangle\langle l|M_\gamma|0\rangle}{(\omega_{n0}{}^2-\omega_1{}^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_1\omega_{l0}-\omega_2\omega_{n0})\right.$$
$$\left.-\frac{\langle 0|X_\alpha|n\rangle\langle n|X_\lambda|l\rangle\langle l|M_\gamma|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_2(\omega_{n0}+\omega_{l0})+\omega_1\omega_{l0})-\frac{\langle 0|X_\alpha|n\rangle\langle n|X_\lambda|l\rangle\langle l|M_\gamma|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_1(\omega_{n0}+\omega_{l0})+\omega_2\omega_{l0})\right]. \quad (4.7)$$

If we set $\omega_1=0$, $\omega_2=\omega$, in the second term of Table I, the result, $B_\gamma\times\Gamma_{\alpha\gamma\lambda}(0,\omega)$ is $i\omega$ times the part of the linear polarizability tensor in a static magnetic field which causes the Faraday rotation.[5] Similarly for term (3) with $\omega_2=0$.

The fourth term represents the curl of the density of magnetic moments induced at frequency $\omega_1+\omega_2$. It is

$$\Sigma_{\alpha\sigma\gamma\delta}{}^{(\omega_1,\omega_2)}=\left(\frac{2}{\hbar^2}\right)\epsilon_{\alpha\sigma\lambda}\sum_l\sum_n\left[\frac{\langle 0|X_\gamma|n\rangle\langle n|M_\lambda|l\rangle\langle l|X_\delta|0\rangle}{(\omega_{n0}{}^2-\omega_2{}^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{l0}\omega_2-\omega_{n0}\omega_1)\right.$$
$$\left.+\frac{\langle 0|M_\lambda|n\rangle\langle n|X_\delta|l\rangle\langle l|X_\gamma|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{l0}(\omega_1+\omega_2)+\omega_{n0}\omega_1)+\frac{\langle 0|M_\lambda|n\rangle\langle n|X_\gamma|l\rangle\langle l|X_\delta|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_2{}^2)}((\omega_1+\omega_2)\omega_{l0}+\omega_2\omega_{n0})\right], \quad (4.8)$$

where $\epsilon_{\alpha\sigma\lambda}$ is the Levi-Civita tensor.

Terms 5 and 6 in the table come from the rate of change of the expectation of $\mathbf{X}$ due to the perturbations $-\mathbf{E}\cdot\mathbf{X}$ and $\nabla\mathbf{E}\cdot\mathbf{Q}$. We find

$$\Delta_{\alpha\gamma\delta\lambda}{}^{(\omega_2,\omega_1)}=\left(\frac{2i}{\hbar^2}\right)(\omega_1+\omega_2)\sum_l\sum_n\left[\frac{\langle 0|X_\lambda|n\rangle\langle n|X_\alpha|l\rangle\langle l|Q_{\gamma\delta}|0\rangle}{(\omega_{n0}{}^2-\omega_1{}^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_{l0}\omega_{n0}-\omega_1\omega_2)\right.$$
$$\left.+\frac{\langle 0|X_\alpha|n\rangle\langle n|X_\lambda|l\rangle\langle l|Q_{\gamma\delta}|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_{n0}\omega_{l0}+(\omega_1+\omega_2)\omega_2)+\frac{\langle 0|X_\alpha|n\rangle\langle n|Q_{\gamma\delta}|l\rangle\langle l|X_\lambda|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{n0}\omega_{l0}+(\omega_1+\omega_2)\omega_1)\right]. \quad (4.9)$$

The last term in Table I is the time rate of change of the divergence of the electric quadrupole density, induced by $-\mathbf{E}\cdot\mathbf{X}$. We find

$$\Lambda_{\alpha\beta\gamma\lambda}{}^{(\omega_1,\omega_2)}=\left(\frac{2i}{\hbar^2}\right)(\omega_1+\omega_2)\sum_l\sum_n\left[\frac{\langle 0|X_\lambda|n\rangle\langle n|Q_{\alpha\beta}|l\rangle\langle l|X_\gamma|0\rangle}{(\omega_{n0}{}^2-\omega_1{}^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_{n0}\omega_{l0}-\omega_1\omega_2)\right.$$
$$\left.+\frac{\langle 0|Q_{\alpha\beta}|n\rangle\langle n|X_\gamma|l\rangle\langle l|X_\lambda|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_2{}^2)}(\omega_{n0}\omega_{l0}+(\omega_1+\omega_2)\omega_2)+\frac{\langle 0|Q_{\alpha\beta}|n\rangle\langle n|X_\lambda|l\rangle\langle l|X_\gamma|0\rangle}{(\omega_{n0}{}^2-(\omega_1+\omega_2)^2)(\omega_{l0}{}^2-\omega_1{}^2)}(\omega_{n0}\omega_{l0}+(\omega_1+\omega_2)\omega_1)\right]. \quad (4.10)$$

The sum of terms (2), (3), (5) and (6) calculated for a one-electron harmonic oscillator should be identical with (2.8) multiplied by $i(\omega_1+\omega_2)$. This is indeed the case. Terms (4) and (7) are not included in (2.8) because this expression is the result of calculating $(i(\omega_1+\omega_2))^{-1}\langle\mathbf{J}(\mathbf{R})\rangle^{(2)}{}_{\omega_1+\omega_2}$ rather than

$$(i(\omega_1+\omega_2))^{-1}\langle\mathbf{J}(\mathbf{R})^{\mathrm{K}}\rangle^{(2)}{}_{\omega_1+\omega_2}.$$

The forms of the terms in column one of Table I evidently confirms the conjectures made in Sec. 1 about the possible types of vector products which make up quadratic polarization in media with inversion symmetry. Terms (2), (3), and (4) correspond to the first ("Faraday") term on the right of (1.1), and (5), (6) and (7) to the second ("quadrupole") term on the right of (1.1), though terms (4) and (7) of the table represent effects not described in Sec. 1.

Our calculation predicts the experimentally observed phase relations between the symmetry-dependent and independent parts of the quadratic polarization. For real wave functions, $\mathbf{X}$ and $\mathbf{Q}$ have real matrix elements, and the orbital part of $\mathbf{M}$ has imaginary matrix elements. The spin part of $\mathbf{M}$ makes no contribution to $\mathbf{J}(\mathbf{R})^{\mathrm{K}}$, in the terms enumerated in Table I.[10] Therefore, we see by inspection that Γ is imaginary, Σ, Δ, and Λ are real and ρ is real. Thus, the polarization due to terms (2) through (7), which is present whether or not

[10] Each term of the quadratic polarization contains products of three matrix elements $\langle 0|A|l\rangle\langle l|B|n\rangle\langle n|C|0\rangle$. From Table I, we find that at most one of the operators contains the total spin operator (through M). If we have zero spin-orbit coupling, the states are products of orthonormal spin and space functions, and the two operators which do not contain the spin leave the spin part of the state $|0\rangle$ unchanged. Since $\langle 0|\mathbf{S}|0\rangle=0$, all matrix elements of $\mathbf{S}$ which appear in these expressions vanish.

there is inversion symmetry, is $\pi/2$ out of phase with that due to the first term, in accordance with experiment.[4]

Since $\mathbf{X}$, $\mathbf{Q}$, and $\mathbf{M}$ are sums of one-electron operators, if Slater-determinant wave functions are used, (4.6) through (4.10) may be expressed in terms of matrix elements of the component one-electron functions. In this case, the excited many-electron states, $|n\rangle$, will each have one excited "conduction electron" and one excited "hole." The terms of (4.6)–(4.10) will have, as factors, matrix elements between different hole states as well as between electron states.

ACKNOWLEDGMENT

I am grateful to P. J. Price for suggesting this problem and for helpful discussions.

APPENDIX

Let the electromagnetic potentials in the conventional gauge be

$$\mathbf{A}'=\sum_a A_a \exp i(\omega_a t-\mathbf{K}_a\cdot\mathbf{r})+\text{c.c.},$$
$$\phi'=0, \tag{A1}$$

where the $\mathbf{A}_a$ are constant vectors $\perp\mathbf{K}_a$. The sum is over Maxwell waves with electric fields $(i\omega_a/c)\mathbf{A}_a$ and magnetic fields $-i\mathbf{K}_a\times\mathbf{A}_a$.

We transform to a new gauge (A,ϕ) given by

$$\begin{aligned}A_\alpha(\mathbf{R},\mathbf{r}')&=A_\alpha'-\nabla_\alpha'\{(r_\beta' A_\beta')\\&\quad-\tfrac{1}{2}r_\beta'(A_\beta'-\nabla_\beta r_\gamma' A_\gamma')\}\\&=\tfrac{1}{2}(\mathbf{r}'\times\mathbf{B})_\alpha+\tfrac{1}{2}r_\beta' r_\gamma'\nabla_\alpha'\nabla_\beta' A_\gamma',\end{aligned} \tag{A2}$$

$$\begin{aligned}\phi(\mathbf{R},r')&=(1/c)(d/dt)(r_\beta' r_\alpha'\nabla_\beta' A_\alpha'-r_\alpha' A_\alpha')\\&=-r_\alpha'(E_\alpha-\tfrac{1}{2}r_\beta'\nabla_\beta' E_\alpha).\end{aligned} \tag{A3}$$

On substituting (A1) and (A3) in the scalar potential term of (3.3b), expanded in powers of $\mathbf{K}\cdot\mathbf{r}'$ to first order, it becomes

$$\begin{aligned}q\phi(\mathbf{R},\mathbf{r}_i')=q\sum_a[&-\mathbf{r}_i'\cdot\mathbf{E}_a(1-\tfrac{1}{2}i\mathbf{K}_a\cdot\mathbf{r}_i')\\&\times\exp i(\omega t-\mathbf{K}_a\cdot\mathbf{R}+\theta_a)\\&+\text{Hermitian conjugate}].\end{aligned} \tag{A4}$$

The first term in [ ] of (3.3b) is of first order in $\langle p\rangle/mc$, so that we need only consider the zeroth power in its expansion in powers of $\mathbf{K}\cdot\mathbf{r}'$:

$$\begin{aligned}&-(q/2mc)\textstyle\sum_\alpha\{p_{i,\alpha},A_\alpha(\mathbf{R},\mathbf{r}_i')\}\\&\quad=-(q/2mc)\textstyle\sum_a\mathbf{B}_a\cdot(\mathbf{r}_i'\times\mathbf{p}_i)\\&\qquad\times\exp i(\omega_a t-\mathbf{K}_a\cdot\mathbf{R}+\theta_a)+\text{H.c.}\end{aligned} \tag{A5}$$

The second term on the right of (A2) has been neglected because it is of order $K^2\langle r\rangle^2$.

The last term in the square bracket of (3.3b) is quadratic in the field and gives mixing effects when taken as a first-order perturbation. Comparing the part of the expectation value of an operator, G, to second order in the perturbation $-q\mathbf{r}'\cdot\mathbf{E}$ with the part of first order in $(q^2/2mc^2)(\mathbf{r}'\times\mathbf{B})^2$, we find that the latter is smaller by a factor of order $\Delta E/mc^2$, where ΔE is a representative excitation energy of the system. We can therefore neglect the term $(2mc^2)^{-1}(q\mathbf{A})^2$ in our gauge, since $\Delta E/mc^2\sim10^{-6}$ and $K\langle r\rangle\sim10^{-3}$.

To first order in $K\langle r\rangle$ and $\langle p\rangle/mc$, (3.3b) becomes

$$\begin{aligned}H'=\textstyle\sum_{\mathbf{R}}\sum_a[&-\mathbf{X}\cdot\mathbf{E}_a+i\mathbf{K}_a\cdot\mathbf{Q}\cdot\mathbf{E}_a-\mathbf{B}_a\cdot\mathbf{M}]\\&\times\exp i(\mathbf{K}_a\cdot\mathbf{R}+\theta_a+\omega_a t)+\text{H.c.},\end{aligned} \tag{3.7}$$

where

$$\mathbf{X}=\textstyle\sum_j q\mathbf{r}_j',\quad \mathbf{Q}=\frac{1}{2}\sum_j q\mathbf{r}_j'\mathbf{r}_j',$$
$$\mathbf{M}=(q/2mc)\textstyle\sum_j(\mathbf{L}_j+\hbar\boldsymbol{\sigma}_j).$$

The fourth term of (3.5) is of first order in the field; thus, we must investigate its expectation value in first-order perturbation theory. With $-q\mathbf{E}\cdot\mathbf{r}$ as the perturbation, the expectation of this term in first order is smaller than that of $q d\mathbf{r}/dt$ in second order by a factor $\Delta E/mc^2\sim10^{-6}$, which is $\sim10^{-3}$ times $K\langle r\rangle$. Since $K\sim\omega/c$ and $\langle\boldsymbol{\sigma}\rangle\sim1$, the fifth term of (3.5) is smaller than the term of zero order in $K\langle r\rangle$ by a factor $\hbar\omega/mc^2\sim10^{-6}$ at optical frequencies. The sixth term in (3.5) also contains a factor which makes it $\sim10^{-6}$ smaller than the term of zeroth order in $K\langle r\rangle$. The last term is $\sim\hbar\omega/mc^2$ smaller than the third term in (3.5) and may also be neglected. Thus we need consider only the first three terms in (3.5).