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SELF-CONSISTENT FIELD THEORY OF LINEAR AND NONLINEAR CRYSTALLINE DIELECTRICS INCLUDING LOCAL FIELD EFFECTS*

by

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ABSTRACT

The linear and nonlinear responses of a crystalline dielectric to external fields are derived using a self-consistent field formulation. Local field effects arising from the rapidly varying charge density in a lattice are built into the analysis in order to identify properly the effect of the lattice on the macroscopic dielectric tensors. Formal solutions are obtained for a general lattice; standard results are deduced for special cases ranging from point dipoles to a free electron gas. The nonlinear terms, to second order, are then used as a basis to solve the dual problem of optical harmonic and subharmonic generation.

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I. INTRODUCTION

In this paper we formulate the linear and nonlinear dielectric properties of a crystal by the self-consistent field (SCF) technique. The SCF theory was developed by Nozières and Pines[1] and Ehrenreich and Cohen[2] to study electron-electron interactions via a dielectric formalism. The latter paper discusses some of the consequences of a lattice, particularly the use of Bloch, instead of free, electrons in the matrix elements. More recently, Adler[3] and Wiser[4] have shown that the Bloch representation leads to a local field theory— one in which the fields vary appreciably over a lattice constant. Their results for the linear response of nonuniform systems evolve from a coulomb interaction. Adler generalizes the gauge to include the electromagnetic fields directly and, in the nonlocal field limit, extends the Ehrenreich and Cohen results to obtain transverse effects. Herein we find this gauge convenient and natural to describe the reaction of nonuniform media to impressed electric fields. The theory is made gauge invariant so that we do not lose the collective electron behavior. Further we carry the results to nonlinear terms. Nonlinear susceptibilities have been studied by Armstrong et al.,[5] but the local field effects have been handled in an ad hoc manner; our description includes the lattice in a more consistent way.

The electron motion is treated by applying the density matrix to a one-electron, periodic-plus-self-consistent potential Hamiltonian. The SCF is contributed by the external field and all the dipoles in the lattice. Fields that enter Maxwell's equations are then obtained from the SCF by suitably averaging the local fields over a unit cell. From these macroscopic fields, we define linear and nonlinear dielectric tensors which give the appropriate macroscopic behavior of the crystal.

In this paper we attempt to strike a balance between formal solutions and familiar results. For this reason we dwell at length on the limits of the free electron gas, the point dipole, and the nonlocal field approximation. The free electron limit yields the plasma oscillation and an indication that this plasma-dependent term vanishes at low temperatures for all but extremely long wavelengths. Conductivity in the anomalous skin effect region is also correctly given by this derivation. The nonlocal field limit exhibits a quasi-free "effective mass" plasma oscillation plus the usual result for polarizability in a Bloch representation. The point dipole limit predicts a generalized Lorenz-Lorentz law which reduces to the familiar law for cubic symmetry.

We then proceed to solve a sample nonlinear problem by the method of Green's functions. The generality of this method for solving coupled mode problems is emphasized.

II. NOTATION

We consider a rigid crystal lattice of volume Ω and unit cell volume Δ. Direct lattice vectors are denoted $\underset{\sim}{x}_\ell$ where the origin is set at a particular lattice site and ℓ is some other site; reciprocal lattice vectors are denoted $\underset{\sim}{G}$ where $\underset{\sim}{G} \cdot \underset{\sim}{x}_\ell = 2\pi \times$ integer.

The one-electron, SCF Hamiltonian consists of an unperturbed part, H_o, and a perturbation caused by the self-consistent potential

$$H(\underset{\sim}{x}, t) = H_o(\underset{\sim}{x}) + V(\underset{\sim}{x}, t) \tag{1}$$

where $H_o = (p^2/2m) + V_o(\underset{\sim}{x})$, the periodic Bloch Hamiltonian. The perturbation in an applied electromagnetic field is given by

$$V(\underset{\sim}{x}, t) = -\frac{e}{2mc}(\underset{\sim}{A}(\underset{\sim}{x}, t)\cdot \underset{\sim}{p} + \underset{\sim}{p}\cdot \underset{\sim}{A}(\underset{\sim}{x}, t)) + \frac{e^2}{2mc^2}\, \underset{\sim}{A}(\underset{\sim}{x}, t)\cdot \underset{\sim}{A}(\underset{\sim}{x}, t) \tag{2}$$

where we cannot arbitrarily assume that $\underset{\sim}{A}$, the vector potential, is

transverse. We have chosen a gauge in which the scalar potential, $ev(\underset{\sim}{x})$, vanishes; however, longitudinal effects are retained as shown in Appendix A by a gauge-invariant choice of current density defined in Section IV.

Quantities such as $V(\underset{\sim}{x}, t)$ are defined as the local (microscopic) values for any point $\underset{\sim}{x}$ in the lattice. The corresponding macroscopic quantities are obtained by averaging over a unit cell. If we denote the macroscopic position variable of a certain cell as $\underset{\sim}{X}$ and the macroscopic function as $\overline{V}(\underset{\sim}{X}, t)$ for example, and if we expand the local function in a "reduced zone" Fourier series ($|\underset{\sim}{q}| <$ any nonzero $|\underset{\sim}{G}|$) such as

$$V(\underset{\sim}{x}, t) = \sum_{\underset{\sim}{q}\underset{\sim}{G}\omega} V(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \exp\left[i((\underset{\sim}{q} + \underset{\sim}{G})\cdot \underset{\sim}{x} - \omega t)\right] ,$$ then we have by

averaging over the cell at $\underset{\sim}{X}$ and assuming $|\underset{\sim}{q}| << |\underset{\sim}{G}|$

$$\overline{V}(\underset{\sim}{X}, t) \equiv \sum_{\underset{\sim}{q}\underset{\sim}{G}} V(\underset{\sim}{q}, \underset{\sim}{G}, t)\, \Delta^{-1} \int_{\Delta_{\underset{\sim}{X}}} \exp\left[i(\underset{\sim}{q} + \underset{\sim}{G})\cdot \underset{\sim}{x}\, d^3x\right]$$

$$\simeq V(\underset{\sim}{q}, 0, t) \exp i\, \underset{\sim}{q}\cdot \underset{\sim}{X} . \qquad (3)$$

We have factored out the slowly varying $\exp i\, \underset{\sim}{q}\cdot \underset{\sim}{x}$ from the integrand leaving only the $\underset{\sim}{G} = 0$ term to contribute Δ upon integration. The subscript on the integral indicates the volume over which we integrate. Therefore we may equate the Fourier expansion coefficients of the macroscopic function with the $\underset{\sim}{G} = 0$ coefficients of the microscopic function's expansion. The Fourier series employed above presumes periodic boundary conditions on the lattice and periodic time variations. Neither of these assumptions is essential, but it is more convenient to write sums instead of Fourier integrals. The inverse transform is, of course,

$$V(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = (2\pi\Omega)^{-1} \int_{\Omega} d^3x \int_{-\infty}^{+\infty} dt\, V(\underset{\sim}{x}, t) \exp\left[-i((\underset{\sim}{q} + \underset{\sim}{G})\cdot \underset{\sim}{x} - \omega t)\right] .$$

Fourier transforms, inverses, and macroscopic-microscopic relations are defined similarly for all quantities of interest.

The exact and unperturbed Hamiltonians have sets of complete orthonormal eigenfunctions designated as $|m]$ and $|\underset{\sim}{k}\gamma\rangle = \varphi_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$ respectively. $H|m] = \epsilon_m|m]$ and $H_o|\underset{\sim}{k}\gamma\rangle = \epsilon_{\underset{\sim}{k}\gamma}|\underset{\sim}{k}\gamma\rangle$. $\varphi_{\underset{\sim}{k}\gamma}$ stands for the Bloch wavefunctions in the reduced zone scheme, that is $\varphi_{\underset{\sim}{k}\gamma}(\underset{\sim}{x}) = \Omega^{-1/2} \exp(i\,\underset{\sim}{k}\cdot\underset{\sim}{x})\, u_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$ where $\underset{\sim}{k}$ is defined over the first Brillouin zone and γ is a band index. $u_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$, which we symbolize as $\Delta^{-1/2}|\underset{\sim}{k}\gamma)$, is periodic in the lattice and forms a complete orthonormal set of functions defined over the unit cell. In addition $\epsilon_{\underset{\sim}{k}\gamma} = \epsilon_{\underset{\sim}{k}+\underset{\sim}{G}\gamma}$ and $u_{\underset{\sim}{k}+\underset{\sim}{G}\gamma}(\underset{\sim}{x}) = \exp(-i\,\underset{\sim}{G}\cdot\underset{\sim}{x})\, u_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$ as shown by Kittel,[6] Chapter 9.

We next define a density operator $\rho(\underset{\sim}{x}, t) \equiv \sum_m |m]\, P_m\, [m|$ where P_m is the ensemble average probability of state $|m]$ being occupied. This operator obeys the Liouville equation $i\hbar\dot{\rho} = [H, \rho]$ and consists of the sum of an equilibrium part, ρ_o, and a perturbed part, $\rho_1(\underset{\sim}{x}, t)$. ρ_o is diagonal in the Bloch representation; its eigenvalue is the statistical distribution function which we take to be the Fermi-Dirac function, $f_o(\epsilon_{\underset{\sim}{k}\gamma}) = [\exp((\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_f)/kT) + 1]^{-1}$.

III. THE LORENTZ TENSOR

As is the rule when discussing the dielectric behavior of a medium we treat the electromagnetic field classically and the lattice quantum mechanically. The classical relation between the electric field and induced polarization, $\underset{\sim}{P}(\underset{\sim}{x}, t)$, is characterized by the Lorentz tensor as denoted by Born[7] and Born and Wolf.[8] The polarization is obtained in terms of the SCF by quantum methods in the next section.

The electric field, $\underset{\sim}{E}(\underset{\sim}{x}, t)$, measured at any point in the lattice is the sum of 1) the incident vacuum field, $\underset{\sim}{E}^{(i)}(\underset{\sim}{k}_o) \exp(i(\underset{\sim}{k}_o\cdot\underset{\sim}{x} - \omega t))$, where $k_o = \omega/c$, 2) the contribution from the polarization field of the medium over a volume bounded by the outer surface of the lattice, Σ, and the surface,

σ, of a small sphere of radius b surrounding the point $\underset{\sim}{x}$, and 3) the depolarization field of the polarized material within the sphere. The depolarization field, $\underset{\sim}{E}^{(\sigma)}(\underset{\sim}{x}, t)$, is the familiar $-(4\pi/3)\underset{\sim}{P}(\underset{\sim}{x}, t)$ when b becomes smaller than any nonuniformity in the polarization. Since we eventually allow $b \longrightarrow 0$, this case is always obtained except if a point dipole exists at $\underset{\sim}{x}$, in which circumstance one must subtract off the reaction field of the point dipole in question. For the present we take the polarization as continuous, and in the section on point dipoles we consider the complication in detail.

The field contributed at $\underset{\sim}{x}$ by the polarization density in a volume d^3x' about the point $\underset{\sim}{x}'$ is given by $\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \{\underset{\sim}{P}(\underset{\sim}{x}', t - R/c)d^3x'/R\}$ where $R = |\underset{\sim}{x} - \underset{\sim}{x}'|$ and the operator $\underset{\sim}{\nabla}$ acts on the coordinate $\underset{\sim}{x}$. Thus the total field is

$$\underset{\sim}{E}(\underset{\sim}{x}, t) = \underset{\sim}{E}^{(i)}(\underset{\sim}{k}_o)\exp(i(\underset{\sim}{k}_o \cdot \underset{\sim}{x} - \omega t) - \frac{4\pi}{3}\underset{\sim}{P}(\underset{\sim}{x}, t) + \int_{\sigma}^{\Sigma} d^3x' \, \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\{\underset{\sim}{P}(\underset{\sim}{x}', t - R/c)/R\}. \tag{4}$$

We consider the time dependence of all fields to be $\exp(-i\omega t)$ so that the retardation factor in the integral yields the function $F(R) = \exp(i\omega R/c)/R$. The time dependence can now be factored out, and we state (with reference to Born and Wolf,[8] Appendix 5) that as $b \longrightarrow 0$,

$$\int_{\sigma}^{\Sigma} d^3x' \, \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\{\underset{\sim}{P}(\underset{\sim}{x}', \omega)F(R)\} \longrightarrow -(8\pi/3)\underset{\sim}{P}(\underset{\sim}{x}, \omega) + \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\int_{\sigma}^{\Sigma} d^3x' \, \underset{\sim}{P}(\underset{\sim}{x}', \omega)F(R).$$

The first term on the right combines with the depolarization field to give $-4\pi \, \underset{\sim}{P}(\underset{\sim}{x}, \omega)$. We now expand the field and polarization in the reduced zone Fourier series

$$\sum_{\underset{\sim}{q}\underset{\sim}{G}}^{\Sigma}(\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) + 4\pi \, \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)) \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x} = \underset{\sim}{E}^{(i)}(\underset{\sim}{k}_o) \exp i\underset{\sim}{k}_o\cdot\underset{\sim}{x}$$

$$+ \sum_{\underset{\sim}{q}\underset{\sim}{G}}^{\Sigma} \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\int_{\sigma}^{\Sigma} d^3x' \, \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)F(R) \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}'. \tag{5}$$

If we note that $\nabla^2 F(R) + (\omega/c)^2 F(R) = -4\pi\,\delta(R)$ (= 0 over the range of integration) and that $[\,\nabla^2 + (\underset{\sim}{q} + \underset{\sim}{G})^2]\ \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x} = 0$, we may use Green's theorem to convert the integral in (5) to a surface integral. That is, since

$$F(R)\ \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}' = \frac{[\exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}'\ \nabla^2 F(R) - F(R)\ \nabla^2(\exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}')]}{[\,(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2]},$$

we integrate by parts to obtain

$$\sum_{\underset{\sim}{q}\underset{\sim}{G}} (\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) + 4\pi\,\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega))\ \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x} = \underset{\sim}{E}^{(i)}(\underset{\sim}{k}_o)\ \exp i\underset{\sim}{k}_o\cdot\underset{\sim}{x}$$

$$+ \sum_{\underset{\sim}{q}\underset{\sim}{G}} \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \int_\sigma^\Sigma d\underset{\sim}{s}'\cdot \Big\{ (\partial F(R)/\partial\underset{\sim}{n}')\ \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}'$$

$$- F(R)\ \partial(\exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot x')/\partial\underset{\sim}{n}' \Big\}\ /\ [(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2] \qquad (6)$$

where $d\underset{\sim}{s}'$ is a surface element on σ or Σ and $\partial/\partial\underset{\sim}{n}'$ represents the outward gradient at that element. The surface integral at σ when $b\longrightarrow 0$ yields only $4\pi\ \exp i(\underset{\sim}{q} + \underset{\sim}{G})\cdot\underset{\sim}{x}/[(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2]$ because of the singularities in the functions $F(R)$ and $\partial F(R)/\partial\underset{\sim}{n}'$ as $R\longrightarrow 0$. At the outer surface, Σ, these latter functions propagate with the vacuum speed of light and must combine with the incident field $\underset{\sim}{E}^{(i)}(\underset{\sim}{k}_o)$ to produce extinction. In other words, for (6) to be true at all points of space-time we require

$$\underset{\sim}{E}^{(i)}(k_o)\ \exp i\underset{\sim}{k}_o\cdot\underset{\sim}{x} = -\ \sum_{\underset{\sim}{q}\underset{\sim}{G}} \underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \int_\sigma^\Sigma d\underset{\sim}{s}'\cdot \Big\{ \cdots \Big\}\ /[(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2]\ .$$

Eliminating the incident-extinction field combination and noting $\underset{\sim}{\nabla}\times\underset{\sim}{\nabla}\times = \underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\ ) - \nabla^2$, we evaluate (6) as $b\longrightarrow 0$, and obtain upon inverse

transforming

$$\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = 4\pi \left[(\omega/c)^2 \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) - (\underset{\sim}{q} + \underset{\sim}{G})(\underset{\sim}{q} + \underset{\sim}{G})\cdot \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)\right] / \left[(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2\right]. \tag{7}$$

Now if we identify as macroscopic fields the $\underset{\sim}{G} = 0$ term in the expansion as discussed in Section II, and if we introduce the index of refraction, $n = q^2/(\omega/c)^2$, we get $\overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) = (4\pi/(n^2 - 1))[\overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega) - n^2 \hat{q}\,\hat{q}\cdot \overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega)]$ where $\hat{q}$ is the unit $\underset{\sim}{q}$ vector. The dot product of this equation with $\hat{q}$ gives $\hat{q}\cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) + 4\pi \hat{q}\cdot \overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega) = 0$. But we recognize in this the displacement vector $\overline{\underset{\sim}{D}}(\underset{\sim}{q}, \omega) = \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) + 4\pi \overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega)$; so the above is simply $\underset{\sim}{\nabla}\cdot \overline{\underset{\sim}{D}}(\underset{\sim}{x}, \omega) = 0$, and our equation is consistent with Maxwell's in a medium with no net charge.

If we then let $\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega)\,\delta_{0\underset{\sim}{G}} + \underset{\sim}{L}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)\cdot \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$, we have from (7) the definition of the Lorentz tensor, $\underset{\sim}{L}$, in component form.

$$\left[\underset{\sim}{L}(\underset{\sim}{q}, \underset{\sim}{G}, \omega\right]_{\mu\nu} = 4\pi(1 - \delta_{0\underset{\sim}{G}})\left[(\omega/c)^2 \delta_{\mu\nu} - (\underset{\sim}{q} + \underset{\sim}{G})_\mu (\underset{\sim}{q} + \underset{\sim}{G})_\nu\right] / \left[(\underset{\sim}{q} + \underset{\sim}{G})^2 - (\omega/c)^2\right]. \tag{8}$$

Obviously the Lorentz tensor is symmetric and vanishes altogether for $\underset{\sim}{G} = 0$.

IV. QUANTUM FORMULATION

From Maxwell's equation $\underset{\sim}{\nabla}\times \underset{\sim}{H} = c^{-1}(\dot{\underset{\sim}{E}} + 4\pi \dot{\underset{\sim}{P}} + 4\pi \underset{\sim}{J})$ we note that if we define a complex current density $\underset{\sim}{j}(\underset{\sim}{x}, t) = \underset{\sim}{J}(\underset{\sim}{x}, t) + \dot{\underset{\sim}{P}}(\underset{\sim}{x}, t)$ and take the Fourier transforms, we may identify $\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \omega^{-1}\,\mathrm{Im}\{\underset{\sim}{j}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)\}$. The complex current density operator may be defined in terms of the exact states, or equivalently, in terms of the unperturbed states with an appropriate density matrix basis.

$$\begin{aligned}\underset{\sim}{j}(\underset{\sim}{x}, t) &= \sum_m P_m \left[\frac{e\hbar}{2mi}\left((\underset{\sim}{\nabla}|m\rangle)\langle m| - |m\rangle(\underset{\sim}{\nabla}\langle m|)\right) - \frac{e^2}{mc}\underset{\sim}{A}(\underset{\sim}{x}, t)|m\rangle\langle m|\right] \\ &\equiv \sum_{\underset{\sim}{k}\underset{\sim}{q}\gamma\gamma'} \left[\frac{e\hbar}{2mi}\left(\varphi^*_{\underset{\sim}{k}\gamma}(\underset{\sim}{\nabla}\varphi_{\underset{\sim}{k}+\underset{\sim}{q}\,\gamma'}) - (\underset{\sim}{\nabla}\varphi^*_{\underset{\sim}{k}\gamma})\varphi_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'}\right) - \frac{e^2}{mc}\underset{\sim}{A}(\underset{\sim}{x}, t)\varphi^*_{\underset{\sim}{k}\gamma}\varphi_{\underset{\sim}{k}+\underset{\sim}{q}\,\gamma'}\right] \\ &\quad \times \langle \underset{\sim}{k} + \underset{\sim}{q}\,\gamma'|\rho(\underset{\sim}{x}, t)|\underset{\sim}{k}\gamma\rangle\,. \end{aligned} \tag{9}$$

We demonstrate in Appendix A that this definition is gauge invariant to terms linear in $\underset{\sim}{A}$ including all the highly local fields. Our entire theory is then invariant under infinitesimal gauge transformations, hence under arbitrary transformations. Thus full longitudinal and transverse effects are recovered without manifestly including a scalar potential.

Equation (9) may be expressed in terms of the Bloch functions described in Section II. If we make use of the periodicity of $u_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$ and $\underset{\sim}{\nabla} u_{\underset{\sim}{k}\gamma}(\underset{\sim}{x})$, by expanding such terms in a Fourier series involving only reciprocal lattice vectors, then we obtain the transform of $\underset{\sim}{j}(\underset{\sim}{x}, t)$ in terms of the reduced matrix elements $(\underset{\sim}{k}\gamma \,|\, B \,|\, \underset{\sim}{k}'\gamma') = \Delta^{-1} \int_{\Delta} d^3x\, u^*_{\underset{\sim}{k}\gamma}\, B\, u_{\underset{\sim}{k}'\gamma'}$ defined over the unit cell. This transform is

$$\underset{\sim}{j}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \Omega^{-1} \sum_{\underset{\sim}{k}\gamma\gamma'} \left\{ \left[\frac{e}{m} (\underset{\sim}{k}\gamma \,|\, (\underset{\sim}{p} + \hbar(\underset{\sim}{k} + (\underset{\sim}{q}+\underset{\sim}{G})/2)) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} \,|\, \underset{\sim}{k}+\underset{\sim}{q}\gamma') \langle \underset{\sim}{k}+\underset{\sim}{q}\gamma' \,|\, \rho(\underset{\sim}{x}, \omega) \,|\, \underset{\sim}{k}\gamma \rangle \right] \right.$$
$$\left. - \left[\sum_{\underset{\sim}{q}'\underset{\sim}{G}'\omega'} \frac{e^2}{mc} \underset{\sim}{A}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}-\underset{\sim}{G}', \omega') (\underset{\sim}{k}\gamma \,|\, e^{-i\underset{\sim}{G}'\cdot\underset{\sim}{x}} \,|\, \underset{\sim}{k}+\underset{\sim}{q}'\gamma') \langle \underset{\sim}{k}+\underset{\sim}{q}'\gamma' \,|\, \rho(\underset{\sim}{x}, \omega-\omega') \,|\, \underset{\sim}{k}\gamma \rangle \right] \right\}. \tag{10}$$

The Liouville equation provides us with the density matrix elements needed in (10). Splitting ρ and H into equilibrium and perturbed parts, we have

$$(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega) \langle \underset{\sim}{k}+\underset{\sim}{q}\gamma' \,|\, \rho_1(\underset{\sim}{x}, \omega) \,|\, \underset{\sim}{k}\gamma \rangle = (f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'}) - f_o(\epsilon_{\underset{\sim}{k}\gamma})) \langle \underset{\sim}{k}+\underset{\sim}{q}\gamma' \,|\, V(\underset{\sim}{x}, \omega) \,|\, \underset{\sim}{k}\gamma \rangle$$
$$+ \sum_{\omega'} \langle \underset{\sim}{k}+\underset{\sim}{q}\gamma' \,|\, [\, \rho_1(\underset{\sim}{x}, \omega'), V(\underset{\sim}{x}, \omega-\omega')] \,|\, \underset{\sim}{k}\gamma \rangle . \tag{11}$$

We have kept the commutator of ρ_1 and V in order to go beyond the usual linear approximation. The zeroth order term in the current density, independent of $\underset{\sim}{A}$ or t is given by

$$\underset{\sim}{j}_o(\underset{\sim}{q}, \underset{\sim}{G}) = \Omega^{-1} \sum_{\underset{\sim}{k}\gamma\gamma'} \frac{e}{m} (\underset{\sim}{k}\gamma \,|\, \underset{\sim}{p} + \hbar(\underset{\sim}{k} + (\underset{\sim}{q}+\underset{\sim}{G})/2)) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} \,|\, \underset{\sim}{k}+\underset{\sim}{q}\gamma') \langle \underset{\sim}{k}+\underset{\sim}{q}\gamma' \,|\, \rho_o \,|\, \underset{\sim}{k}\gamma \rangle . \tag{12}$$

This equilibrium contribution to the current density has the periodicity of the lattice and vanishes identically when H_o has time-reversal symmetry as we show in Appendix B.

Contributions to $\underset{\sim}{j}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ to first and higher order in $\underset{\sim}{A}$ are obtained by substituting (2) and (11) in (10). For expediency we define

$$F_{\gamma'\gamma,\,\omega}^{\underset{\sim}{k}'-\underset{\sim}{k}} = \frac{[f_o(\epsilon_{\underset{\sim}{k}'\gamma'}) - f_o(\epsilon_{\underset{\sim}{k}\gamma})]}{[\epsilon_{\underset{\sim}{k}'\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega]} \ .$$

We now may write down the linear and second order terms by expanding (10) and (11) to the proper order.

$$\underset{\sim}{j}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(e^2/mc\Omega) \sum_{\underset{\sim}{k}\gamma\underset{\sim}{G}'} [f_o(\epsilon_{\underset{\sim}{k}\gamma}) \underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}', \omega)(\underset{\sim}{k}\gamma | e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}} | \underset{\sim}{k}\gamma)$$

$$+ \sum_{\gamma'} (F_{\gamma'\gamma,\,\omega}^{\underset{\sim}{q}}/m)(\underset{\sim}{k}\gamma | (\underset{\sim}{p} + \hbar(\underset{\sim}{k} + (\underset{\sim}{q} + \underset{\sim}{G})/2)) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} | \underset{\sim}{k} + \underset{\sim}{q}\gamma')$$

$$\times (\underset{\sim}{k} + \underset{\sim}{q}\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} \underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}', \omega)\cdot(\underset{\sim}{p} + \hbar(\underset{\sim}{k} + (\underset{\sim}{q} + \underset{\sim}{G}')/2)) | \underset{\sim}{k}\gamma)] \qquad (13)$$

and

$$\underset{\sim}{j}_2(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = (e^3/2m^2c^2\Omega) \sum_{\substack{\underset{\sim}{k}\gamma\gamma\omega' \\ \underset{\sim}{q}'\underset{\sim}{G}'\underset{\sim}{G}''}} \Bigg\{ \Bigg[F_{\gamma'\gamma,\,\omega}^{\underset{\sim}{q}'} (\underset{\sim}{k}\gamma | e^{-i(\underset{\sim}{G}-\underset{\sim}{G}'')\cdot\underset{\sim}{x}} | \underset{\sim}{k}+\underset{\sim}{q}'\gamma') \underset{\sim}{A}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}'', \omega-\omega')$$

$$\times (\underset{\sim}{k}+\underset{\sim}{q}'\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} \underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\cdot(2\underset{\sim}{p} + \hbar(\underset{\sim}{q}' + \underset{\sim}{G}') | \underset{\sim}{k}\gamma) \Bigg]$$

$$+ \Bigg[(\underset{\sim}{k}\gamma | (\underset{\sim}{p} + \hbar(\underset{\sim}{k} + (\underset{\sim}{q} + \underset{\sim}{G})/2)) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} | \underset{\sim}{k} + \underset{\sim}{q}\gamma') [F_{\gamma'\gamma,\,\omega}^{\underset{\sim}{q}}$$

$$\times (\underset{\sim}{k} + \underset{\sim}{q}\gamma' | e^{i(\underset{\sim}{G}'+\underset{\sim}{G}'')\cdot\underset{\sim}{x}} \underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega)\cdot\underset{\sim}{A}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}'', \omega-\omega') | \underset{\sim}{k}\gamma)$$

$$+ \sum_{\gamma''} \left((F_{\gamma'\gamma'',\,\omega'}^{\underset{\sim}{q}'} - F_{\gamma''\gamma,\,\omega-\omega'}^{\underset{\sim}{q}-\underset{\sim}{q}'})/2m(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega) \right)$$

$$\times (\underset{\sim}{k} + \underset{\sim}{q}\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} \underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\cdot \left(2\underset{\sim}{p} + \hbar(\underset{\sim}{q}' + \underset{\sim}{G}') \right) | \underset{\sim}{k} + \underset{\sim}{q} - \underset{\sim}{q}'\gamma'')$$

$$\times (\underset{\sim}{k} + \underset{\sim}{q} - \underset{\sim}{q}'\gamma'' | e^{i\underset{\sim}{G}''\cdot\underset{\sim}{x}} \underset{\sim}{A}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}'', \omega-\omega')\cdot \left(2\underset{\sim}{p} + \hbar(\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{G}'') \right) | \underset{\sim}{k}\gamma)] \Bigg] \Bigg\} \ . \qquad (14)$$

Higher order terms may be similarly iterated.

This time we have reduced the Bloch matrix elements to their periodic form in order to best exhibit the local field nature of the interaction. That is, Fourier components of the field at all reciprocal lattice vectors contribute to the current or polarization density at any particular $\underset{\sim}{G}$. Thus we may have an Umklapp process in which the wavevectors $\underset{\sim}{q}$ are additive only up to a reciprocal lattice vector. Our choice of Bloch functions is appropriate to all periodic structures, but, as we will see in the sections on free electrons and point dipoles, other choices enormously simplify equations (13) and (14).

In our gauge we note that $\underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(ic/\omega)\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$, and we make the connection between polarization and complex current density as previously mentioned. This enables us to express the first and second order polarizations in terms of the electric fields by

$$\underset{\sim}{P}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \sum_{\underset{\sim}{G}'} \underset{\sim}{\alpha}_{\underset{\sim}{G}\underset{\sim}{G}'}(\underset{\sim}{q}, \omega)\cdot \underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}', \omega), \tag{15}$$

$$\underset{\sim}{P}_2(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \sum_{\underset{\sim}{q}'\omega'\underset{\sim}{G}'\underset{\sim}{G}''} \underset{\sim}{\beta}_{\underset{\sim}{G}\underset{\sim}{G}'\underset{\sim}{G}''}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega'):\underset{\sim}{E}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\underset{\sim}{E}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}'', \omega-\omega'). \tag{16}$$

In what follows we drop the Re and Im notation keeping in mind that the imaginary part of the polarization is related to the real current density. The linear and second order polarizability tensors, $\underset{\sim}{\alpha}$ and $\underset{\sim}{\beta}$, are obtained easily from (13) and (14). In cartesian component form then

$$\begin{aligned}[\underset{\sim}{\alpha}_{\underset{\sim}{G}\underset{\sim}{G}'}(\underset{\sim}{q}, \omega)]_{\mu\nu} = -(e^2/m\omega^2\Omega)\sum_{\underset{\sim}{k}\gamma\gamma'} [f_o(\epsilon_{\underset{\sim}{k}\gamma})(\underset{\sim}{k}\gamma|e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)\delta_{\gamma\gamma'}\delta_{\mu\nu} \\ + (F^{\underset{\sim}{q}}_{\gamma'\gamma,\omega}/4m)(\underset{\sim}{k}\gamma|(2\underset{\sim}{p} + \hbar(2\underset{\sim}{k} + \underset{\sim}{q} + \underset{\sim}{G}))_\mu e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}}|\underset{\sim}{k} + \underset{\sim}{q}\gamma') \\ \times(\underset{\sim}{k} + \underset{\sim}{q}\gamma'|e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}}(2\underset{\sim}{p} + \hbar(2\underset{\sim}{k} + \underset{\sim}{q} + \underset{\sim}{G}'))_\nu|\underset{\sim}{k}\gamma)]\end{aligned} \tag{17}$$

and

$$[\underset{\sim}{\beta}_{\underset{\sim}{G}\underset{\sim}{G}'\underset{\sim}{G}''}(\underset{\sim}{q}, \omega ; \underset{\sim}{q}', \omega')]_{\lambda\mu\nu} = (e^3/2m^2\Omega\omega\omega'(\omega - \omega')) \sum_{\underset{\sim}{k}\gamma\gamma'} \left\{ \left[F^{\underset{\sim}{q}}_{\gamma'\gamma, \omega'} \right. \right. \tag{18}$$

$$\times (\underset{\sim}{k}\gamma | e^{-i(\underset{\sim}{G}+\underset{\sim}{G}'')\cdot\underset{\sim}{x}} | \underset{\sim}{k} + \underset{\sim}{q}'\gamma')(\underset{\sim}{k} + \underset{\sim}{q}'\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} (2\underset{\sim}{p} + \hbar(\underset{\sim}{q}' + \underset{\sim}{G}'))_\mu | \underset{\sim}{k}\gamma)\delta_{\lambda\nu} \Big]$$

$$+ \left[(\underset{\sim}{k}\gamma | 2\underset{\sim}{p} + \hbar(2\underset{\sim}{k} + \underset{\sim}{q} + \underset{\sim}{G}))_\lambda e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} | \underset{\sim}{k} + \underset{\sim}{q}\gamma') \left\{ (F^{\underset{\sim}{q}}_{\gamma'\gamma, \omega}/2) \right. \right.$$

$$\times (\underset{\sim}{k} + \underset{\sim}{q}\gamma' | e^{i(\underset{\sim}{G}'+\underset{\sim}{G}'')\cdot\underset{\sim}{x}} | \underset{\sim}{k}\gamma)\delta_{\mu\nu}$$

$$+ \sum_{\gamma''} \left((F^{\underset{\sim}{q}'}_{\gamma'\gamma'', \omega'} - F^{\underset{\sim}{q}-\underset{\sim}{q}'}_{\gamma''\gamma, \omega-\omega'})/2m(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega) \right)$$

$$\times (\underset{\sim}{k}+\underset{\sim}{q}\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} (2\underset{\sim}{p}+\hbar(\underset{\sim}{q}'+\underset{\sim}{G}'))_\mu | \underset{\sim}{k}+\underset{\sim}{q}-\underset{\sim}{q}'\gamma'')(\underset{\sim}{k}+\underset{\sim}{q}-\underset{\sim}{q}'\gamma'' | e^{i\underset{\sim}{G}''\underset{\sim}{x}} (2\underset{\sim}{p}+\hbar(\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{G}''))_\nu | \underset{\sim}{k}\gamma) \Big] \Big] \Big\}$$

The defining relations (15) and (16) explicitly illustrate conservation of energy (frequency) and wavevector (up to a reciprocal lattice vector) for the electron polarization wave interacting with the true fields in the lattice. It is our next task to show how the macroscopic constitutive properties of a crystal are developed from these true polarizabilities.

V. FORMAL RESULTS

With the Lorentz tensor of Section III and the polarizabilities of the previous section, we have the information necessary to compute the macroscopic linear and nonlinear dielectric behavior of the crystal. In order to simplify the formal manipulations though, we assume that the nonlinear polarization is much smaller than the linear. This allows us to write

$$\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \cong \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega)\delta_{0\underset{\sim}{G}} + \underset{\sim}{L}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \cdot \sum_{\underset{\sim}{G}'} \underset{\sim}{\alpha}_{\underset{\sim}{G}\underset{\sim}{G}'}(\underset{\sim}{q}, \omega) \cdot \underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}', \omega). \tag{19}$$

If we define a matrix $\underset{\sim}{S}(\underset{\sim}{q}, \omega)$ whose rows and columns are labelled by the reciprocal lattice vectors and each of whose elements is a second rank tensor given by $[\underset{\sim}{S}(\underset{\sim}{q}, \omega)]_{\underset{\sim}{G}\underset{\sim}{G}'} = \underset{\sim}{L}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \cdot \underset{\sim}{\alpha}_{\underset{\sim}{G}\underset{\sim}{G}'}(\underset{\sim}{q}, \omega)$, we may put (19)

in the form

$$\sum_{\underset{\sim}{G}'} [\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)]_{\underset{\sim}{G}\underset{\sim}{G}'} \cdot \underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}', \omega) = \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega)\, \delta_{0\,\underset{\sim}{G}}. \tag{20}$$

Here $\underset{\sim}{1}$ is the unit matrix of unit second rank tensors. Formally inverting this equation, we have

$$\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}', \omega) = \sum_{\underset{\sim}{G}} [\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)]^{-1}_{\underset{\sim}{G}'\underset{\sim}{G}} \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega)\, \delta_{0\,\underset{\sim}{G}}$$

$$= [\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)]^{-1}_{\underset{\sim}{G}'0} \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega). \tag{21}$$

The process of taking the inverse of this infinite dimensional matrix is not a well-defined mathematical operation. In practice however, $\underset{\sim}{\alpha}$ and $\underset{\sim}{L}$ are rapidly converging functions of reciprocal lattice vectors. The first is because the reduced matrix elements, $(\underset{\sim}{k}\gamma \,|\exp i\underset{\sim}{G}\cdot\underset{\sim}{x}|\, \underset{\sim}{k}'\gamma')$, are an "average" of $\exp i\underset{\sim}{G}\cdot\underset{\sim}{x}$ over the unit cell even for the tightly bound lower bands γ. Thus at large $\underset{\sim}{G}$ the matrix elements become vanishingly small. For this reason one may assume a cutoff $\underset{\sim}{G}$ for the $\underset{\sim}{S}(\underset{\sim}{q}, \omega)$ matrix without losing much of the physics. The inverse of a matrix of the form $\begin{bmatrix} \underset{\sim}{B} & 0 \\ 0 & \underset{\sim}{1} \end{bmatrix}$ where $\underset{\sim}{B}$ is finite and $\underset{\sim}{1}$ is infinite is simply $\begin{bmatrix} \underset{\sim}{B}^{-1} & 0 \\ 0 & \underset{\sim}{1} \end{bmatrix}$. The matrix $\underset{\sim}{B}$ is just $\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)$ for $\underset{\sim}{G}, \underset{\sim}{G}' < \underset{\sim}{G}$ cutoff.

In one important case this argument completely breaks down - that of point dipoles. For then the wavefunctions are so tightly bound that the "averaging" only takes place at the lattice site rather than over the whole unit cell. Therefore, there is no particular predominance of the low $\underset{\sim}{G}$ terms. All is not lost in this case though, as we see in the section on point dipoles, because we effectively evaluate the sum (20) before we have to invert.

Now substituting (21) into (15) and (16) and setting $\underset{\sim}{G} = 0$, we solve for the macroscopic polarizations.

$$\overline{\underset{\sim}{P}}_1(\underset{\sim}{q}, \omega) = \sum_{\underset{\sim}{G}'} \underset{\sim}{\alpha}_{0\underset{\sim}{G}'}(\underset{\sim}{q}, \omega) \cdot \left[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)\right]^{-1}_{\underset{\sim}{G}'0} \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) \tag{22}$$

$$\overline{\underset{\sim}{P}}_2(\underset{\sim}{q}, \omega) = \sum_{\underset{\sim}{q}'\omega'\underset{\sim}{G}'\underset{\sim}{G}''} \underset{\sim}{\beta}_{0\underset{\sim}{G}'\underset{\sim}{G}''}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') : \left\{ \left[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}', \omega')\right]^{-1}_{\underset{\sim}{G}'0} \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}', \omega')\right\}$$

$$\left\{\left[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega')\right]^{-1}_{\underset{\sim}{G}'0} \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega')\right\} \quad . \tag{23}$$

The macroscopic linear dielectric tensor is defined in the usual way

$$\left[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}\right] \cdot \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) = 4\pi \overline{\underset{\sim}{P}}_1(\underset{\sim}{q}, \omega), \tag{24}$$

and the macroscopic, second order polarization susceptibility is defined

$$\overline{\underset{\sim}{P}}_2(\underset{\sim}{q}, \omega) = \sum_{\underset{\sim}{q}'\omega'} \underset{\sim}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') : \overline{\underset{\sim}{E}}(\underset{\sim}{q}', \omega')\, \overline{\underset{\sim}{E}}(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega'), \tag{25}$$

through which we obtain our central results quite simply

$$\left[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}\right] = 4\pi \sum_{\underset{\sim}{G}} \underset{\sim}{\alpha}_{0\underset{\sim}{G}}(\underset{\sim}{q}, \omega) \cdot \left[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}, \omega)\right]^{-1}_{\underset{\sim}{G}0} \tag{26}$$

$$\underset{\sim}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') = \sum_{\underset{\sim}{G}\underset{\sim}{G}'} \underset{\sim}{\beta}_{0\underset{\sim}{G}\underset{\sim}{G}'}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') : \left[\underset{\sim}{1} - \underset{\sim}{S}(q'\omega')\right]^{-1}_{\underset{\sim}{G}0}$$

$$\left[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega')\right]^{-1}_{\underset{\sim}{G}'0} \cdot \tag{27}$$

The tensor quantities $\underset{\sim}{\alpha}$, $\underset{\sim}{\beta}$, $\underset{\sim}{L}$, and $\underset{\sim}{S}$ are given in equations (17), (18), (8), and (20). Now we have a complete formalism which may be applied classically to Maxwell's equations; our only approximations have been in assuming a rigid periodic lattice, in using the one-electron, SCF approach to the many-body problem, and in taking the nonlinear polarization to be much smaller than the linear. Our remaining task is to apply the formalism to problems of interest - namely, free electrons, quasi-free crystal electrons, point dipoles, and nonlinear effects.

VI. FREE ELECTRON GAS

The simplest application of the results of Section V is to the linear dielectric tensor in a free electron gas. The Bloch functions are taken over to the plane wave representation, $|\underset{\sim}{k}\gamma\rangle \longrightarrow |\underset{\sim}{k}\rangle = \Omega^{-1/2} \exp i\underset{\sim}{k}\cdot\underset{\sim}{x}$ and $\epsilon_{\underset{\sim}{k}\gamma} \longrightarrow \epsilon_{\underset{\sim}{k}} = \hbar^2 k^2/2m$. Thus the functions $|\underset{\sim}{k}\gamma)$ are just constants so that the reduced matrix elements give only $(\underset{\sim}{k}\gamma|\ \exp i\underset{\sim}{G}\cdot\underset{\sim}{x}|\underset{\sim}{k}'\gamma') = \delta_{\underset{\sim}{G}0}$ and $(\underset{\sim}{k}\gamma|(\exp i\underset{\sim}{G}\cdot\underset{\sim}{x})\,\underset{\sim}{p}|\underset{\sim}{k}'\gamma') = 0$. We see then from (17) and (26) that $\underset{\sim}{\alpha}_{00}$ is the only surviving term since $[\underset{\sim}{1} - \underset{\sim}{S}(\underset{\sim}{q},\omega)]^{-1}_{00} = \underset{\sim}{1}$ because $\underset{\sim}{L}(\underset{\sim}{q}, 0, \omega) = 0$. The dielectric tensor is easily written in component form

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q},\omega) - \underset{\sim}{1}]_{\mu\nu} = 4\pi\,[\underset{\sim}{\alpha}_{00}(\underset{\sim}{q},\omega)]_{\mu\nu}$$

$$= -(4\pi e^2/m\Omega\omega^2)\sum_{\underset{\sim}{k}}\left[f_o(\epsilon_{\underset{\sim}{k}})\delta_{\mu\nu} + \frac{\hbar^2}{m}\left(\frac{f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}})}{\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}} - \epsilon_{\underset{\sim}{k}} - \hbar\omega}\right)\right.$$

$$\left.\times\,(\underset{\sim}{k} + \underset{\sim}{q}/2)_\mu\,(\underset{\sim}{k} + \underset{\sim}{q}/2)_\nu\right]. \qquad (28)$$

The sum over all $\underset{\sim}{k}$ of the distribution function $f_o(\epsilon_{\underset{\sim}{k}})$ is the number of electrons, N. Defining the plasma frequency $\omega_p^2 = 4\pi e^2 N/m\Omega$, we see that the first term on the right is merely $-(\omega_p^2/\omega^2)\delta_{\mu\nu}$. This is the only contributing term if $\underset{\sim}{q} \longrightarrow 0$ as $\omega \neq 0$. Due to the spherical symmetry of the electron gas, the off-diagonal components of the tensor (28) vanish leaving only two independent components - the longitudinal along $\underset{\sim}{q}$ and the transverse. We write these with a convenient notation

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q},\omega) - \underset{\sim}{1}]_{\left\{\begin{smallmatrix}\text{long.}\\ \text{trans.}\end{smallmatrix}\right\}} = -\,\omega_p^2/\omega^2$$

$$-\,\frac{4\pi e^2}{m\Omega\omega^2}\sum_{\underset{\sim}{k}} q^{-2}\,\frac{f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}})}{\left(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2) - (m\omega/\hbar)\right)}\left\{\begin{matrix}(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2))^2\\ (\underset{\sim}{k}\times\underset{\sim}{q})^2\end{matrix}\right\}. \qquad (29)$$

The longitudinal component may be expressed in a more familiar form if we note the following identities:

$$(\underset{\sim}{k}\cdot\underset{\sim}{q} + q^2/2)^2 \Big/ \left(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2) - (m\omega/\hbar)\right) = \left(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2) + (m\omega/\hbar)\right) + \left[(m\omega/\hbar)^2 \Big/ \left(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2) - (m\omega/\hbar)\right)\right],$$

$$\sum_{\underset{\sim}{k}} f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}}) = 0,$$

$$\sum_{\underset{\sim}{k}} \left(f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}})\right) (\underset{\sim}{k}\cdot\underset{\sim}{q} + q^2/2) \Big/ q^2 = -\sum_{\underset{\sim}{k}} f_o(\epsilon_{\underset{\sim}{k}}) = -N.$$

The last identity is proved by making the substitution $\underset{\sim}{k} + \underset{\sim}{q} \longrightarrow -\underset{\sim}{k}$ and using $f_o(\epsilon_{-\underset{\sim}{k}}) = f_o(\epsilon_{\underset{\sim}{k}})$, the evenness of f_o in $\underset{\sim}{k}$, and the oddness of $\underset{\sim}{k}\cdot\underset{\sim}{q}$ in $\underset{\sim}{k}$. There results then

$$\left[\underset{\sim}{\epsilon}(\underset{\sim}{q},\omega) - \underset{\sim}{1}\right]_{\text{long.}} = -\frac{4\pi e^2 m}{q^2 \Omega \hbar^2} \sum_{\underset{\sim}{k}} \frac{f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}})}{\left(\underset{\sim}{k}\cdot\underset{\sim}{q} + (q^2/2) - (m\omega/\hbar)\right)} \quad . \tag{30}$$

This equation is typically derived[2] from a coulomb interaction, but we have obtained it using a gauge-invariant vector potential.

The dielectric components have interesting properties at low temperatures and at low q. In this region $f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}}) - f_o(\epsilon_{\underset{\sim}{k}}) \cong -\delta(k - k_f)\hat{k}\cdot\underset{\sim}{q}$ for Fermi-Dirac statistics. k_f is the Fermi wavevector. In addition we take the sums over to integrals according to the prescription $\Omega^{-1}\Sigma_{\underset{\sim}{k}} \longrightarrow 2(2\pi)^{-3}\int d^3k$ and we define $\beta = \left((q^2/2) - (m\omega/\hbar)\right)/k_f q$ and $\mu = \hat{k}\cdot\hat{q}$. Making these substitutions in (29) and (30) and integrating trivially over the magnitude of $\underset{\sim}{k}$ and the azimuthal angle about $\underset{\sim}{q}$, we have

$$\left[\underset{\sim}{\epsilon}(\underset{\sim}{q},\omega) - \underset{\sim}{1}\right]_{\text{long.}} = \frac{4\pi e^2 m}{\hbar^2 q^2}\left[\frac{4\pi k_f}{(2\pi)^3}\int_{-1}^{+1} d\mu \frac{\mu}{\mu + \beta + i\alpha}\right] \quad , \tag{31}$$

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]_{trans.} = -\frac{\omega_p^2}{\omega^2} + \frac{4\pi e^2}{m\omega^2}\left[\frac{2\pi k_f^3}{(2\pi)^3}\int_{-1}^{+1} d\mu \, \frac{\mu(1-\mu^2)}{\mu + \beta + i\alpha}\right] . \qquad (32)$$

The quantity $i\alpha$ is added to the denominator to insure convergence when $|\beta| \leq 1$. It may be thought of as arising from an adiabatic switching-on of the vector potential or from a relaxation time, τ, in which case $\alpha = m/\hbar k_f q\tau$. In cases of interest to us we consider α to be very small, and we will take the limit as $\alpha \longrightarrow 0$. No confusion should arise from the new definitions of α, β, and μ in this section since there is no overlap with previous definitions.

The integrals in (31) and (32) are evaluated, setting α to zero afterwards. With $k_s^2 = 4e^2 m k_f/\pi\hbar^2$, the "screening" wavevector, then

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]_{long.} = (k_s^2/q^2)\left[1 - \beta \ell n\left|(\beta + 1)/(\beta - 1)\right|^{1/2}\right] . \qquad (33)$$

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]_{trans.} = -(\omega_p^2/\omega^2)\left[(3/2)(\beta^2 + \beta(1 - \beta^2)\ell n\left|(\beta + 1)/(\beta - 1)\right|^{1/2})\right] . \qquad (34)$$

We see strictly for nonzero q neither longitudinal nor transverse components exhibit a pure plasma oscillation. In fact for the longitudinal dielectric constant we have recovered the Fermi-Thomas result, k_s^2/q^2, with a correction due to finite frequency and the Fermi surface. The apparent singularity in the dielectric constants at $\omega = 0$ and $q = 2k_f$ never occurs because the results (33) and (34) depend on small wavevectors, that is $q << k_f$.

The plasmon limit is asymptotically approached when $|\beta| >> 1$ for which we expand $\ell n\left|(\beta + 1)/(\beta - 1)\right|^{1/2} = \beta^{-1} + (1/3)\beta^{-3} + (1/5)\beta^{-5} + \ldots$. In this domain $\beta \cong -m\omega/\hbar k_f q$ and we have approximately

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]_{long.} \cong -(\omega_p^2/\omega^2)\left[1 + (3/5)(\hbar k_f q/m\omega)^2\right] , \qquad (35)$$

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]_{trans.} \cong -(\omega_p^2/\omega^2)\left[1 + (1/5)(\hbar k_f q/m\omega)^2\right] . \qquad (36)$$

The conductivity tensor of the free electron gas is related to the dielectric tensor by $\underset{\sim}{\sigma}(\underset{\sim}{q}, \omega) = -(\omega/4\pi)\mathrm{Im}[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}]$. In the low temperature, low q region we then find the transverse conductivity from (32). Consider $|\beta| < 1$ and $\alpha \longrightarrow 0$ so the integration is carried out using Cauchy's principal value formula and we obtain

$$[\underset{\sim}{\sigma}(\underset{\sim}{q}, \omega)]_{\text{trans.}} = -(3\omega_p^2/16\omega)\beta(1 - \beta^2). \tag{37}$$

As in equation (34) we have used $N/\Omega = 8\pi k_f^3/3(2\pi)^3$, the result of counting plane wave modes in a Fermi gas. When $(q^2/2) << (m\omega/\hbar)$, we have the conditions appropriate to the anomalous skin effect for which (37) becomes

$$[\underset{\sim}{\sigma}(q, \omega)]_{\text{trans.}} \cong (3\pi e^2 N/4\hbar k_f q\Omega)[1 - (m\omega/\hbar k_f q)^2] . \tag{38}$$

We have obtained the standard result in the first term on the right plus a correction which needs to be less than one but not at all infinitesimal.

VII. NONLOCAL FIELD APPROXIMATION

We have seen in the previous section that the uniform free electron gas rigorously has no local field corrections. It is possible, though not always valid, to ignore such corrections for lattice electrons. Adler[3] and Ehrenreich and Cohen[2] point out many salient features of this approximation. Thus we treat this problem briefly, demonstrating how the free electron plasma and acceleration terms are replaced by "effective mass" plasma oscillations and quasi-atomic polarizability contributed by the core electrons in the long-wavelength limit.

Neglect of the Umklapp processes by setting all $\underset{\sim}{G} = 0$ is what characterizes this approximation. The contributing term in the dielectric tensor is just $4\pi\underset{\sim}{\alpha}_{00}(\underset{\sim}{q},\omega)$. Passing to the dipole limit, $q \longrightarrow 0$, we have from (17)

$$4\pi\,[\underset{\sim}{\alpha}_{00}(0,\omega)]_{\mu\nu} = -4\pi(e^2/m\omega^2\Omega)\sum_{\underset{\sim}{k}\gamma\gamma'}[f_o(\epsilon_{\underset{\sim}{k}\gamma})\delta_{\gamma\gamma'}\delta_{\mu\nu} + (f_o(\epsilon_{\underset{\sim}{k}\gamma'}) - f_o(\epsilon_{\underset{\sim}{k}\gamma}))$$

$$\times((\underset{\sim}{k}\gamma\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma')(\underset{\sim}{k}\gamma'\,|\,p_\nu\,|\,\underset{\sim}{k}\gamma)/m(\epsilon_{\underset{\sim}{k}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega))]\,. \qquad (39)$$

We have used the orthonormality of the $|\underset{\sim}{k}\gamma)$ so that $(\underset{\sim}{k}\gamma\,|\,\underset{\sim}{k}\,|\,\underset{\sim}{k}\gamma') = \underset{\sim}{k}\delta_{\gamma\gamma'}$. The first term under the sum is simply the total number of electrons N, so we again have the plasma term $-(\omega_p^2/\omega^2)$.

Let us now assume that we have an insulator or a semiconductor at low temperatures such that $f_o(\epsilon_{\underset{\sim}{k}\gamma}) = 1$ for all $\gamma \le \Gamma$ and 0 for all $\gamma > \Gamma$. That is, all bands up to Γ are completely filled and all higher are empty. Taking the real part of (39), we have

$$\mathrm{Re}[\,4\pi\underset{\sim}{\alpha}_{00}(0,\omega)]_{\mu\nu} = -(\omega_p/\omega)^2 + (4\pi e^2/m\Omega\omega^2) \qquad (40)$$

$$\times \sum_{\substack{\underset{\sim}{k}\gamma\neq\gamma' \\ \gamma'\le\Gamma}}[1 - H(\Gamma-\gamma)]\,(\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'})\left[\frac{(\underset{\sim}{k}\gamma\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma')(\underset{\sim}{k}\gamma'\,|\,p_\nu\,|\,\underset{\sim}{k}\gamma) + \mathrm{c.c.}}{m\,\left((\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'})^2 - (\hbar\omega)^2\right)}\right],$$

where H is the unit step function and $(\underset{\sim}{k}\gamma\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma') = (\underset{\sim}{k}\gamma'\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma)^*$. We now take advantage of the f-sum rule for Bloch states as given by Wilson,[9] p. 47.

$$(m/\hbar^2)\,[\partial^2\epsilon_{\underset{\sim}{k}\gamma'}/\partial k_\mu\,\partial k_\nu] = \delta_{\mu\nu}$$

$$- \sum_{\gamma\neq\gamma'}\left((\underset{\sim}{k}\gamma\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma')(\underset{\sim}{k}\gamma'\,|\,p_\nu\,|\,\underset{\sim}{k}\gamma) + \mathrm{c.c.}\right)\Big/ m(\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'}).$$

Inserting the sum rule in (40) we have finally

$$\mathrm{Re}\,[4\pi\underset{\sim}{\alpha}_{00}(0,\omega)]_{\mu\nu} = -(4\pi e^2/\hbar^2\Omega\omega^2)\sum_{\underset{\sim}{k}\gamma'\le\Gamma}[\partial^2\epsilon_{\underset{\sim}{k}\gamma'}/\partial k_\mu\,\partial k_\nu] \qquad (41)$$

$$+\frac{4\pi e^2}{m^2\Omega\omega^2}\sum_{\substack{\underset{\sim}{k}\gamma\neq\gamma' \\ \gamma'\le\Gamma}}\left[\frac{(\hbar\omega)^2}{\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'}} - H(\Gamma-\gamma)(\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'})\right]\left[\frac{(\underset{\sim}{k}\gamma\,|\,p_\mu\,|\,\underset{\sim}{k}\gamma')(\underset{\sim}{k}\gamma'\,|\,p_\nu\,|\,\underset{\sim}{k}\gamma) + \mathrm{c.c.}}{(\epsilon_{\underset{\sim}{k}\gamma} - \epsilon_{\underset{\sim}{k}\gamma'})^2 - (\hbar\omega)^2}\right].$$

The free electron plasma oscillation has been cancelled, and we have instead an "effective mass" plasma oscillation indicated by the first term on the right. For the tightly bound lower states $\epsilon_{\underset{\sim}{k}\gamma}$ is relatively independent of $\underset{\sim}{k}$ and the upper states have balancing contributions from positive and negative effective masses, thus filled bands produce negligible plasma response. In a metal we would sum the intraband term over the conduction band electrons as well, obtaining a quasi-free effective mass plasma oscillation. The second sum on the right hand side of (41) is the interband contribution and is usually cited as the optical polarizability in a Bloch representation. The optical designation is our dipole approximation.

VIII. POINT DIPOLES

The complicated matrix formulation in Section V may be greatly simplified when the lattice consists of an array of point dipoles. We assume that the charge of the medium is completely localized at the lattice sites. This limit is pertinent to the usual derivation of the Lorenz-Lorentz law and takes full account of the local field effects.

For the purpose of evaluating the linear and nonlinear polarizability tensors we return to the general complex current density, equation (9), and propose, in place of the Bloch functions, a more appropriate representation for the unperturbed wavefunctions. For the tight binding case the functions with the required symmetry are given by

$$\varphi_{\underset{\sim}{k}\gamma} = \Omega^{-1/2} \sum_{\underset{\sim}{x}_\ell} (\exp i\underset{\sim}{k}\cdot\underset{\sim}{x}_\ell)\, d_\gamma(\underset{\sim}{x} - \underset{\sim}{x}_\ell).$$

The function $d_\gamma(\underset{\sim}{x} - \underset{\sim}{x}_\ell)$ is suitably centralized about lattice site ℓ; depending on the degree of binding, we may think of it as a Wannier function (a superposition of Bloch functions within band γ) or an atomic eigenfunction designated by the state label γ. In our case, however, we think of $d_\gamma(\underset{\sim}{x} - \underset{\sim}{x}_\ell)$ as zero everywhere but at $\underset{\sim}{x} = \underset{\sim}{x}_\ell$. This δ-function character of the d_γ, together with their orthonormality in the unit cell, allows us to evaluate the relevant matrix elements quite simply.

$$\langle \underset{\sim}{k}\gamma \,|\, V(\underset{\sim}{x}) \,|\, \underset{\sim}{k}'\gamma' \rangle = (\Delta/\Omega) \sum_{\underset{\sim}{x}_\ell} (\exp i(\underset{\sim}{k}' - \underset{\sim}{k})\cdot \underset{\sim}{x}_\ell)\, V(\underset{\sim}{x}_\ell)\, \delta_{\gamma\gamma'}.$$

$$\langle \underset{\sim}{k}\gamma \,|\, V(\underset{\sim}{x})\underset{\sim}{p} \,|\, \underset{\sim}{k}'\gamma' \rangle = (\Delta/\Omega) \sum_{\underset{\sim}{x}_\ell} (\exp i(\underset{\sim}{k}' - \underset{\sim}{k})\cdot \underset{\sim}{x}_\ell)\, V(\underset{\sim}{x}_\ell)\, \underset{\sim}{p}_{\gamma\gamma'}.$$

$$\underset{\sim}{p}_{\gamma\gamma'} = \Delta^{-1} \int_\Delta d_\gamma{}^*(\underset{\sim}{x} - \underset{\sim}{x}_\ell)\underset{\sim}{p}\, d_{\gamma'}(\underset{\sim}{x} - \underset{\sim}{x}_\ell)\, d^3x = \underset{\sim}{p}_{\gamma'\gamma}{}^*.$$

If we note the property of the crystal Kronecker delta, $\delta(\underset{\sim}{k} - \underset{\sim}{G}') = (\Delta/\Omega)\sum_{\underset{\sim}{x}_\ell} (\exp i\underset{\sim}{k}\cdot\underset{\sim}{x}_\ell)$, that is $\underset{\sim}{k}$ must be a reciprocal lattice vector to survive the lattice sum, we may calculate the various orders of the current density transform similarly to (13) and (14). Using the above matrix elements we have

$$\underset{\sim}{j}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(e^2N/mc\Omega) \sum_{\underset{\sim}{G}'} \underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}', \omega) \tag{42}$$

$$-(e^2/m^2c\Omega) \sum_{\underset{\sim}{k}\gamma\gamma'\underset{\sim}{G}'} F^{\underset{\sim}{q}}_{\gamma'\gamma,\omega}\, \underset{\sim}{p}_{\gamma\gamma'}\, \underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}', \omega)\cdot\left(\underset{\sim}{p}_{\gamma'\gamma} + (\hbar/2)(\underset{\sim}{q} + \underset{\sim}{G}')\,\delta_{\gamma'\gamma}\right)$$

and

$$\underset{\sim}{j}_2(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = (e^3/m^2c^2\Omega) \sum_{\substack{\underset{\sim}{k}\gamma\gamma'\omega' \\ \underset{\sim}{q}'\underset{\sim}{G}'\underset{\sim}{G}''}} \Bigg\{ \Bigg[\Bigg(F^{\underset{\sim}{q}'}_{\gamma'\gamma,\omega'}\delta_{\gamma\gamma'} \left(\underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\cdot\left(\underset{\sim}{p}_{\gamma'\gamma} + (\hbar/2)(\underset{\sim}{q}' + \underset{\sim}{G}')\delta_{\gamma'\gamma}\right)\right)$$

$$\times \underset{\sim}{A}(\underset{\sim}{q} - \underset{\sim}{q}', \underset{\sim}{G}'', \omega - \omega') \Bigg) + \left(F^{\underset{\sim}{q}}_{\gamma'\gamma,\omega}\delta_{\gamma\gamma'}(\underset{\sim}{p}_{\gamma\gamma'}/2) \left(\underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\cdot\underset{\sim}{A}(\underset{\sim}{q} - \underset{\sim}{q}', \underset{\sim}{G}'', \omega - \omega') \right) \right) \Bigg]$$

$$+ \Bigg[\sum_{\gamma''} \left((F^{\underset{\sim}{q}'}_{\gamma'\gamma'',\omega'} - F^{\underset{\sim}{q}-\underset{\sim}{q}'}_{\gamma''\gamma,\omega-\omega'})\underset{\sim}{p}_{\gamma\gamma'}/m(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega) \right)$$

$$\times \left(\underset{\sim}{A}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\cdot\left(\underset{\sim}{p}_{\gamma'\gamma''} + (\hbar/2)(\underset{\sim}{q}' + \underset{\sim}{G}')\delta_{\gamma'\gamma''}\right) \right)$$

$$\times \left(\underset{\sim}{A}(\underset{\sim}{q} - \underset{\sim}{q}', \underset{\sim}{G}'', \omega - \omega')\cdot\left(\underset{\sim}{p}_{\gamma''\gamma} + (\hbar/2)(\underset{\sim}{q} - \underset{\sim}{q}' + \underset{\sim}{G}'')\delta_{\gamma''\gamma}\right) \right) \Bigg] \Bigg\}. \tag{43}$$

A further consequence of the point dipole model is that the energy is relatively independent of the wavevector, and we will take in what follows the limits $\epsilon_{\underset{\sim}{k}\gamma} \longrightarrow \epsilon_{\gamma}$, $F^{\underset{\sim}{q}}_{\gamma'\gamma,\omega} = \left(f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'}) - f_o(\epsilon_{\underset{\sim}{k}\gamma})\right) \Big/ (\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma} - \hbar\omega) \longrightarrow \left(f_o(\epsilon_{\gamma'}) - f_o(\epsilon_{\gamma})\right) \Big/ (\epsilon_{\gamma'} - \epsilon_{\gamma} - \hbar\omega) = F_{\gamma'\gamma,\omega}$. Therefore all terms in (42) and (43) involving $\delta_{\gamma\gamma'}$, $\delta_{\gamma'\gamma''}$, and $\delta_{\gamma''\gamma}$ disappear since $F_{\gamma'\gamma,\omega}\,\delta_{\gamma\gamma'} = 0$ etc. That the cross product term in the last square brackets in (43) vanishes is easily seen by exchanging the dummy indices $\omega' \longleftrightarrow \omega - \omega'$ and $\underset{\sim}{q}'+\underset{\sim}{G}' \longleftrightarrow \underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{G}''$. The remaining sums over $\underset{\sim}{k}$ produce N_c, the number of unit cells. Identifying as before the electric field with the vector potential and the polarization with the current density, we have the polarizability relations

$$\underset{\sim}{P}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \underset{\sim}{\alpha}(\omega) \cdot \sum_{\underset{\sim}{G}'} \underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}', \omega) \tag{44}$$

$$\underset{\sim}{P}_2(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \sum_{\omega'} \underset{\sim}{\beta}(\omega, \omega') : \sum_{\underset{\sim}{q}'\underset{\sim}{G}'\underset{\sim}{G}''} \underset{\sim}{E}(\underset{\sim}{q}', \underset{\sim}{G}', \omega')\underset{\sim}{E}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{G}'', \omega-\omega') \tag{45}$$

where

$$[\underset{\sim}{\alpha}(\omega)]_{\mu\nu} = -(e^2/m\omega^2\Omega)\,[N\delta_{\mu\nu} + (N_c/m) \sum_{\gamma\gamma'} F_{\gamma'\gamma,\omega} (\underset{\sim}{p}_{\gamma\gamma'})_{\mu}\,(\underset{\sim}{p}_{\gamma'\gamma})_{\nu}] \tag{46}$$

$$[\underset{\sim}{\beta}(\omega, \omega')]_{\lambda\mu\nu} = (e^3 N_c/m^3\Omega\,\omega\omega'(\omega-\omega')) \sum_{\gamma\gamma'\gamma''} [(F_{\gamma'\gamma'', \omega'} - F_{\gamma''\gamma, \omega-\omega'})$$

$$\times (\underset{\sim}{p}_{\gamma\gamma'})_{\lambda} (\underset{\sim}{p}_{\gamma'\gamma''})_{\mu} (\underset{\sim}{p}_{\gamma''\gamma})_{\nu} / (\epsilon_{\gamma'} - \epsilon_{\gamma} - \hbar\omega)] \,. \tag{47}$$

A comparison with equations (15) through (18) illustrates the reduction of complexity which this model affords. In contrast to the general lattice polarizability tensors, there is now no dependence on reciprocal lattice vectors. We will see shortly how this is a necessary consequence of the point dipole assumption.

The plasma oscillation, indicated by the first term on the right in (46), is cancelled exactly by the use of a sum rule. This sum rule exists since we take the d_γ to be a complete set of states within the unit cell of eigenvalue ϵ_γ when operated on by the periodic Hamiltonian. By a simple calculation, exactly analogous to the f-sum rule for free atom states, we can show $\delta_{\mu\nu} = \sum_{\gamma \neq \gamma'} \left((\underset{\sim}{p}_{\gamma\gamma'})_\mu (\underset{\sim}{p}_{\gamma'\gamma})_\nu + \text{c.c.} \right) / m(\epsilon_\gamma - \epsilon_{\gamma'})$. The plasma contribution is eliminated when we include this in (46). For this case there would be no residual effective mass plasma oscillation because energies do not depend on $\underset{\sim}{k}$.

Inversion symmetry in the lattice requires the wavefunctions to have a definite parity. In such a circumstance $\underset{\sim}{\beta}$ must vanish since it involves an odd number of parity changes between the same initial and final state. Again, this is a particular of the model since in our general form, (18), higher order multipole moments in the expansion of $\exp i\underset{\sim}{q}\cdot\underset{\sim}{x}$ would not violate parity and $\underset{\sim}{\beta}$ need not vanish.

We have obtained the true polarization in terms of the local field. Now we must make the field self-consistent as we did in Section III by a modification of the Lorentz tensor. This modification is the removal of the reaction field of a particular dipole when considering the effective field acting on that dipole.

Let us consider a classical wave of oscillating point dipoles in the lattice

$$\sum_{\underset{\sim}{q}\underset{\sim}{G}\omega} \underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \exp i((\underset{\sim}{q}+\underset{\sim}{G})\cdot\underset{\sim}{x}-\omega t) = \sum_{\underset{\sim}{q}\underset{\sim}{x}_\ell\omega} (\underset{\sim}{p}_o/\Delta)\, \delta(\underset{\sim}{x}-\underset{\sim}{x}_\ell) \exp i(\underset{\sim}{q}\cdot\underset{\sim}{x} - \omega t). \quad (48)$$

Here $\underset{\sim}{p}_o$ is the dipole moment at each lattice site; we assume only one species of dipole for convenience. From the property of the lattice sum

$\sum_{\underset{\sim}{x}_\ell} \delta(x-x_\ell) = \sum_{\underset{\sim}{G}} \exp i\underset{\sim}{G}\cdot\underset{\sim}{x}$, we have that $\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega) = (\underset{\sim}{p}_o/\Delta)$; indeed the Fourier coefficients of $\underset{\sim}{P}(\underset{\sim}{x}, t)$ are independent of $\underset{\sim}{G}$ as we found quantum mechanically in (44) and (45).

The electric field from the wave (48) may be found in terms of the Hertz potential, $\underset{\sim}{\Pi}$, which in turn satisfies the wave equation. The field is

$$\underset{\sim}{E}(\underset{\sim}{x}, t) = \underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\underset{\sim}{\Pi}(\underset{\sim}{x}, t)) - c^{-2}\,\partial^2\underset{\sim}{\Pi}(\underset{\sim}{x}, t)/\partial t^2. \tag{49}$$

Two alternative solutions may be obtained for the Hertz vector. From Born,[7] Section 75, we have

$$\underset{\sim}{\Pi}(\underset{\sim}{x}, t) = \sum_{\underset{\sim}{q}\underset{\sim}{G}\omega} 4\pi\,\underset{\sim}{\overline{P}}(\underset{\sim}{q}, \omega)\exp i((\underset{\sim}{q}+\underset{\sim}{G})\cdot\underset{\sim}{x} - \omega t)/\left[(\underset{\sim}{q}+\underset{\sim}{G})^2 - (\omega/c)^2\right], \tag{50}$$

and from the retarded potential formulation in Born and Wolf,[8] Chapter 2, we see

$$\underset{\sim}{\Pi}(\underset{\sim}{x}, t) = \sum_{\underset{\sim}{q}\underset{\sim}{x}_\ell\omega} \Delta\,\underset{\sim}{\overline{P}}(\underset{\sim}{q}, \omega)\exp i(\underset{\sim}{q}\cdot\underset{\sim}{x}_\ell - \omega(t-|\underset{\sim}{x}-\underset{\sim}{x}_\ell|/c))/|\underset{\sim}{x}-\underset{\sim}{x}_\ell|. \tag{51}$$

The solution (50) when inserted in (49) leads identically to the result we have already obtained in equation (7) if we remove the $\underset{\sim}{G}$ dependence from $\underset{\sim}{P}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$. Thus it is seen from (51) that our earlier results contain a singularity if $\underset{\sim}{x}$ is at any lattice site. This singularity is just the reaction field of the dipole which we want to remove. Let us take the origin at some arbitrary lattice site; this is allowed by translational symmetry in the lattice. Then we subtract the dipole at $\underset{\sim}{x}_\ell = 0$ from (51) denoting this by a prime on the sum over $\underset{\sim}{x}_\ell$. Now we insert (51) into (49) performing the indicated operations, Fourier analyze the field, inverse time transform, and set $\underset{\sim}{x} = 0$; we obtain

$$\begin{aligned}\sum_{\underset{\sim}{q}\underset{\sim}{G}}\underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = {} & \sum_{\underset{\sim}{q}\underset{\sim}{x}_\ell}{}' \Delta\exp i(\underset{\sim}{q}\cdot\underset{\sim}{x}_\ell + \omega|\underset{\sim}{x}_\ell|/c) \\ & \times\left\{\left[\left(\frac{3}{|\underset{\sim}{x}_\ell|^5} - \frac{3i\omega/c}{|\underset{\sim}{x}_\ell|^4} - \frac{(\omega/c)^2}{|\underset{\sim}{x}_\ell|^3}\right)\underset{\sim}{x}_\ell\left(\underset{\sim}{x}_\ell\cdot\underset{\sim}{\overline{P}}(\underset{\sim}{q}, \omega)\right)\right]\right. \\ & \left.-\left[\left(\frac{1}{|\underset{\sim}{x}_\ell|^3} - \frac{i\omega/c}{|\underset{\sim}{x}_\ell|^2} - \frac{(\omega/c)^2}{|\underset{\sim}{x}_\ell|}\right)\underset{\sim}{\overline{P}}(\underset{\sim}{q}, \omega)\right]\right\}.\end{aligned} \tag{52}$$

Now (52) is fully equivalent to (7) with the singularity properly handled. This is the total effective SCF acting on the dipole at $\underset{\sim}{x} = 0$ with the incident-extinction fields already eliminated.

If we make the same identification of the macroscopic terms as we did in equation (7), we see that we may write (52) as

$$\sum_{\underset{\sim}{q}\underset{\sim}{G}} \underset{\sim}{E}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = \sum_{\underset{\sim}{q}} \overline{\underset{\sim}{E}}(\underset{\sim}{q}, \omega) + \sum_{\underset{\sim}{q}} \underset{\sim}{L}^{(d)}(\underset{\sim}{q}, \omega) \cdot \overline{\underset{\sim}{P}}(\underset{\sim}{q}, \omega)$$

which results in the dipole Lorentz tensor

$$\left[\underset{\sim}{L}^{(d)}(\underset{\sim}{q}, \omega)\right]_{\mu\nu} = 4\pi(q_\mu q_\nu - (\omega/c)^2)/(q^2 - (\omega/c)^2)$$

$$+ \sum_{\underset{\sim}{x}_\ell}{}' \Delta \exp i(\underset{\sim}{q}\cdot\underset{\sim}{x}_\ell + \omega x_\ell/c) \left[\left((3/x_\ell{}^5) - (3i\omega/x_\ell{}^4 c) - (\omega^2/x_\ell{}^3 c^2)\right)(\underset{\sim}{x}_\ell)_\mu (\underset{\sim}{x}_\ell)_\nu \right.$$

$$\left. - \left((1/x_\ell{}^3) - (i\omega/x_\ell{}^2 c) - (\omega^2/x_\ell c^2)\right)\delta_{\mu\nu}\right] . \qquad (53)$$

Again we assume that the nonlinear polarization is small compared to the linear. With the dipole Lorentz tensor and the polarizabilities as given in (46) and (47), we may easily obtain the macroscopic constitutive tensors according to the definitions (24) and (25).

$$[\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega) - \underset{\sim}{1}] = 4\pi \underset{\sim}{\alpha}(\omega)\cdot[\underset{\sim}{1} - \underset{\sim}{L}^{(d)}(\underset{\sim}{q}, \omega)\cdot\underset{\sim}{\alpha}(\omega)]^{-1} \qquad (54)$$

$$\underset{\sim}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') = \underset{\sim}{\beta}(\omega, \omega'):[\underset{\sim}{1} - \underset{\sim}{L}^{(d)}(\underset{\sim}{q}', \omega')\cdot\underset{\sim}{\alpha}(\omega')]^{-1}$$

$$[\underset{\sim}{1} - \underset{\sim}{L}^{(d)}(\underset{\sim}{q} - \underset{\sim}{q}', \omega - \omega')\cdot\underset{\sim}{\alpha}(\omega - \omega')]^{-1} . \qquad (55)$$

The infinite matrix inversion encountered in Section V is completely avoided; we have only to invert a three dimensional tensor. These are the central results for the point dipole lattice at arbitrary wavevector and frequency.

The long wavelength, low frequency limits of (54) are referred to as the generalized Lorentz-Lorenz law. From (53) we see that the dipole Lorentz tensor in this case is simply

$$[\underset{\sim}{L}^{(d)}(0,0)]_{\mu\nu} = (4\pi\delta_{\mu\nu}/3) + \sum_{\underset{\sim}{x}_\ell}{}' \Delta\left[\left(3(\underset{\sim}{x}_\ell)_\mu (\underset{\sim}{x}_\ell)_\nu / x_\ell{}^5\right) - (\delta_{\mu\nu}/x_\ell{}^3)\right] . \quad (56)$$

The first term on the right is the limit of $q_\mu q_\nu / q^2$ as $\underset{\sim}{q} \longrightarrow 0$, a condition of uniform spherical symmetry. This equation is applicable to a crystal of any symmetry where the lattice enters the calculation through the sum $\sum_{\underset{\sim}{x}_\ell}{}'$. Such a sum is a well known and often calculated quantity. In particular, if the lattice site has tetrahedral symmetry, the sum vanishes identically as demonstrated by Born and Huang,[10] Chapter II § 9. This condition obtains for a simple cubic lattice and $\underset{\sim}{L}^{(d)}(0,0) = (4\pi/3)\,\underset{\sim}{1}$.

Cubic symmetry also permits the polarizability tensor (46) to be a multiple of the unit tensor. Therefore the linear dielectric tensor reduces to a scalar given by $[\epsilon(0,0) - 1] = 4\pi\alpha(0)/(1 - 4\pi\alpha(0)/3)$. This is the usual statement of the Lorentz-Lorenz law for isotropic media.

Before proceeding, we say a few words about the appropriateness of the local field correction. We have seen that the criterion for the local field is the degree to which charge is localizable within the medium. For the perfectly uniform distribution as in a free electron gas there is no correction. It is absolutely wrong to apply a density-of-dipoles criterion to determine whether or not local field effects actually exist. In a rarefied medium such as an atomic or molecular gas, the correction is fully appropriate; it is, however, unimportant since $\underset{\sim}{\alpha}$ is so small. The polarizability is small because our definition of $\underset{\sim}{\alpha}$ involves N_{atoms}/Ω, the density of the gas.

IX. NONLINEAR EFFECTS; GREEN'S FUNCTIONS APPLIED TO COUPLED MODE THEORY

In Section V we obtained a second order polarization in a macroscopic frame for which Maxwell's equations apply. We will now drop the bar notation for macroscopic quantities since we will stay entirely in that realm. Maxwell's equations in a nonmagnetic medium ($\mu = 1$) are

$$\underset{\sim}{\nabla} \times \underset{\sim}{E}(\underset{\sim}{x}, t) = c^{-1} \dot{\underset{\sim}{H}}(\underset{\sim}{x}, t) \tag{57}$$

$$\underset{\sim}{\nabla} \times \underset{\sim}{H}(\underset{\sim}{x}, t) = c^{-1} [\dot{\underset{\sim}{E}}(\underset{\sim}{x}, t) + 4\pi(\dot{\underset{\sim}{P}}_1(\underset{\sim}{x}, t) + \dot{\underset{\sim}{P}}_2(\underset{\sim}{x}, t))] \tag{58}$$

to terms second order in the fields. From these we obtain the wave equation in a nonlinear medium

$$\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times \underset{\sim}{E}(\underset{\sim}{x}, t) = -c^{-2} [\ddot{\underset{\sim}{E}}(\underset{\sim}{x}, t) + 4\pi(\ddot{\underset{\sim}{P}}_1(\underset{\sim}{x}, t) + \ddot{\underset{\sim}{P}}_2(\underset{\sim}{x}, t))] \ . \tag{59}$$

If we expand the field and polarizations in a Fourier series in $\exp i(\underset{\sim}{q} \cdot \underset{\sim}{x} - \omega t)$, perform the $\partial^2/\partial t^2$ operation, and use the definitions of the macroscopic constitutive tensors in (24) and (25), we may write after inverse time transforming

$$\sum_{\underset{\sim}{q}} \underset{\sim}{O}(\underset{\sim}{x}, \underset{\sim}{q}, \omega) \cdot \underset{\sim}{E}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q} \cdot \underset{\sim}{x} = \sum_{\underset{\sim}{q}} \underset{\sim}{\Delta}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q} \cdot \underset{\sim}{x}. \tag{60}$$

Here we have taken the "unperturbed" operator as

$$\underset{\sim}{O}(\underset{\sim}{x}, \underset{\sim}{q}, \omega) = [(\underset{\sim}{\nabla} \times \underset{\sim}{\nabla} \times\ ) - (\omega/c)^2 \underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega)] , \tag{61}$$

and the "perturbation" as

$$\underset{\sim}{\Delta}(\underset{\sim}{q}, \omega) = 4\pi(\omega/c)^2 \sum_{\underset{\sim}{q}'\omega'} \underset{\sim}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega') : \underset{\sim}{E}(\underset{\sim}{q}', \omega') \underset{\sim}{E}(\underset{\sim}{q} - \underset{\sim}{q}', \omega - \omega'). \tag{62}$$

The operator $\underset{\sim}{Q}$ describes the propagation of light in a linear, anisotropic dielectric, and the operator $\underset{\sim}{\Delta}$ may be considered as a coupling by a non-linear susceptibility between the various normal modes of the linear medium.

We now introduce the Green's function in second rank tensor form and its Fourier transform according to

$$\underset{\sim}{G}(\underset{\sim}{x} - \underset{\sim}{x}', \omega) = (2\pi)^{-3} \int_{-\infty}^{+\infty} d^3\eta \, \underset{\sim}{G}(\underset{\sim}{\eta}, \omega) \exp i\underset{\sim}{\eta}\cdot(\underset{\sim}{x} - \underset{\sim}{x}'). \tag{63}$$

Multiplying on the right by a unit vector $\hat{u}$ in an arbitrary direction and then operating on the left with $\underset{\sim}{Q}$, we have

$$\underset{\sim}{Q}(\underset{\sim}{x}, \underset{\sim}{q}, \omega)\cdot \underset{\sim}{G}(\underset{\sim}{x} - \underset{\sim}{x}', \omega)\cdot\hat{u} = \tag{64}$$

$$(2\pi)^{-3}\int_{-\infty}^{+\infty} d^3\eta[\eta^2\underset{\sim}{1} - \underset{\sim}{\eta}(\underset{\sim}{\eta}\cdot\ ) - (\omega/c)^2\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega)] \cdot \underset{\sim}{G}(\underset{\sim}{\eta}, \omega)\cdot\hat{u} \exp i\underset{\sim}{\eta}\cdot(\underset{\sim}{x}-\underset{\sim}{x}').$$

We see that if we take

$$[\underset{\sim}{G}(\underset{\sim}{\eta}, \omega)]^{-1} = [\eta^2\underset{\sim}{1} - \underset{\sim}{\eta}(\underset{\sim}{\eta}\cdot\ ) - (\omega/c)^2\underset{\sim}{\epsilon}(\underset{\sim}{q}, \omega)], \tag{65}$$

we would have

$$\underset{\sim}{Q}(\underset{\sim}{x}, \underset{\sim}{q}, \omega)\cdot \underset{\sim}{G}(\underset{\sim}{x}-\underset{\sim}{x}', \omega)\cdot\hat{u} = (2\pi)^{-3}\int_{-\infty}^{+\infty} d^3\eta \exp i\underset{\sim}{\eta}\cdot(\underset{\sim}{x}-\underset{\sim}{x}')\hat{u} = \hat{u}\,\delta(\underset{\sim}{x}-\underset{\sim}{x}') \tag{66}$$

which, of course, is the desired property of a Green's function. It is our basic objective to invert equation (65) and obtain the Fourier transform of the Green's function. Assuming that we can do this and defining a solution to the homogeneous equation by

$$\underset{\sim}{Q}(\underset{\sim}{x}, \underset{\sim}{q}, \omega)\cdot \underset{\sim}{E}^{(0)}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x} = 0, \tag{67}$$

we see that a solution to the general equation (60) is $\underset{\sim}{E}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x}$ where

$$\underset{\sim}{E}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x} - \underset{\sim}{E}^{(0)}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x}$$

$$= (2\pi)^{-3}\int_{-\infty}^{+\infty} d^3\eta \quad d^3x' \underset{\sim}{G}(\underset{\sim}{\eta}, \omega)\cdot \sum_{\underset{\sim}{q}'\omega'} \underset{\sim}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}', \omega'):\underset{\sim}{E}(\underset{\sim}{q}', \omega')\underset{\sim}{E}(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega')$$

$$\times 4\pi(\omega/c)^2 \exp i(\underset{\sim}{\eta}\cdot(\underset{\sim}{x}-\underset{\sim}{x}') + \underset{\sim}{q}\cdot\underset{\sim}{x}'). \qquad (68)$$

That this equation is true is easily proved by operating on the left with $\underset{\sim}{Q}(\underset{\sim}{x}, \underset{\sim}{q}, \omega)$ and summing over $\underset{\sim}{q}$.

This solution is exact and it couples exact waves in modes $(\underset{\sim}{q}', \omega')$ and $(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega')$ to $(\underset{\sim}{q}, \omega)$. However we have just turned the differential equation (60) into an integral equation. The real advance made is that the equation now lends itself to an iterative solution. This is accomplished by entering the homogeneous solution into the integral, thus obtaining a first order correction which one may reinsert etc. The complete form (68) is also useful in the event that only a few modes have significant amplitude. In the next section we work a particular case by the iterative procedure.

X. OPTICAL HARMONIC AND SUBHARMONIC GENERATION

We wish to solve equation (68) by iteration for the simple case of optical harmonic and subharmonic generation. Two zeroth order waves are assumed to be present initially at frequencies ω and 2ω; in first order these give rise to waves at 4ω, 3ω, 2ω, ω, 0. We are going to consider only the waves resulting at ω and 2ω; as we will see later one can suppress the other waves relative to the desired ones by a phase matching technique.

Since the electric fields must be real, we have $\underset{\sim}{E}(\underset{\sim}{q}, \omega) = \underset{\sim}{E}^*(-\underset{\sim}{q}, -\omega)$. The homogeneous solution at ω has wavevector $\underset{\sim}{q}_1$ and the wave at 2ω has wavevector $\underset{\sim}{q}_2$. Then to first order equation (68) yields

$$\underset{\sim}{E}^{(1)}(\underset{\sim}{q}, \omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x} - \underset{\sim}{E}^{(0)}(\underset{\sim}{q}_1, \omega) \exp i\underset{\sim}{q}_1\cdot\underset{\sim}{x}$$

$$= (2\pi)^{-3}\int_{-\infty}^{+\infty} d^3\eta \int d^3x' \underset{\sim}{G}(\underset{\sim}{\eta}, \omega)\cdot \sum_{\underset{\sim}{q}_2} \underset{\approx}{\chi}(\underset{\sim}{q}, \omega; \underset{\sim}{q}_2, 2\omega):\underset{\sim}{E}^{(0)}(\underset{\sim}{q}_2, 2\omega)\underset{\sim}{E}^{(0)*}(\underset{\sim}{q}_2-\underset{\sim}{q}, \omega)$$

$$\times 4\pi(\omega/c)^2 \exp i(\underset{\sim}{\eta}\cdot(\underset{\sim}{x} - \underset{\sim}{x}') + \underset{\sim}{q}\cdot\underset{\sim}{x}'), \qquad (69)$$

$$\underset{\sim}{E}^{(1)}(\underset{\sim}{q}, 2\omega) \exp i\underset{\sim}{q}\cdot\underset{\sim}{x} - \underset{\sim}{E}^{(0)}(\underset{\sim}{q}_2, 2\omega) \exp i\underset{\sim}{q}_2\cdot\underset{\sim}{x}$$

$$= (2\pi)^{-3}\int_{-\infty}^{+\infty} d^3\eta \int d^3x' \underset{\sim}{G}(\underset{\sim}{\eta}, 2\omega)\cdot \sum_{\underset{\sim}{q}_1} \underset{\approx}{\chi}(\underset{\sim}{q}, 2\omega; \underset{\sim}{q}_1, \omega):\underset{\sim}{E}^{(0)}(\underset{\sim}{q}_1, \omega)\underset{\sim}{E}^{(0)}(\underset{\sim}{q}-\underset{\sim}{q}_1, \omega)$$

$$\times 16\pi(\omega/c)^2 \exp i(\underset{\sim}{\eta}\cdot(\underset{\sim}{x} - \underset{\sim}{x}') + \underset{\sim}{q}\cdot\underset{\sim}{x}'). \qquad (70)$$

These equations are still replete with tensor component summations; so it pays to specialize to a particular geometry and material to reduce the algebra. As an illustrative choice we take the material to be KH_2PO_4(KDP); we take ω to correspond to ruby laser radiation at 6943 Å; and we take a flat slab of the crystal of length ℓ in the z direction and infinite in the x and y directions. The crystal axes (designated by superscript $^{(c)}$) are oriented such that the optic axis, $z^{(c)}$, is located in the x - z plane at an angle ψ_o from the z-axis and the angle between $x^{(c)}$ and y is φ_o. Figure 1 gives the geometry.

We arbitrarily assume that there is propagation only along the z-axis, that is $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ have only z components. Such collinear propagation is only a mathematical convenience; physically the wave normals need not be so highly restricted. We are aided by this restriction in that the sums over $\underset{\sim}{q}'$ disappear in (68) since for a given direction of propagation there are at most two possible wavevectors in such a negative uniaxial crystal. In order to reduce complication further, we choose our zeroth order field polarizations to be pure ordinary for the wave at ω and pure extraordinary for the wave at 2ω. From Figure 1 we see that

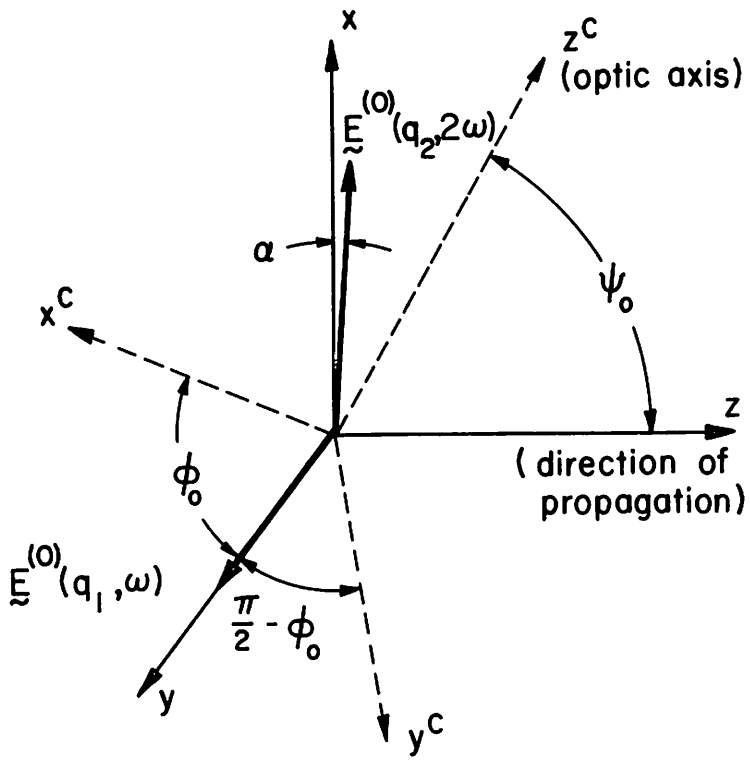

Fig. 1. Axis orientation.

$\underset{\sim}{E}^{(0)}(\underset{\sim}{q}_1, \omega)$ is along the y axis and $\underset{\sim}{E}^{(0)}(\underset{\sim}{q}_2, 2\omega)$ is confined to the x - z plane; the latter will generally not be transverse to the wavevector but will incline at an angle, α, from the x-axis.

Since, by edict, all $\underset{\sim}{q}$ are z-directed, we will drop the vector notation and write q for the z-component. The only x' and y' dependence in the integrals (69) and (70) thus arises from the term exp $i\underset{\sim}{\eta}\cdot(\underset{\sim}{x}-\underset{\sim}{x}')$ which may be integrated over dx'dy' to give $\delta(\eta_x)\delta(\eta_y)$. Then integrating these out we are left with η_z only, which we will denote η. We have remaining

$$\underset{\sim}{E}^{(1)}(q, \omega) \exp iqz - \underset{\sim}{E}^{(0)}(q, \omega) \exp iq_1 z$$

$$= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\eta \int dz' \underset{\sim}{G}(\eta, \omega) \cdot \underset{\approx}{\chi}(q, \omega; q_2, 2\omega) : \underset{\sim}{E}^{(0)}(q_2, 2\omega) \underset{\sim}{E}^{(0)*}(q_2 - q, \omega)$$

$$\times 4\pi(\omega/c)^2 \exp i(\eta(z - z') + qz'), \tag{71}$$

$$\underset{\sim}{E}^{(1)}(q, 2\omega) \exp iqz - \underset{\sim}{E}^{(0)}(q_2, 2\omega) \exp iq_2 z$$

$$= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\eta \int dz' \underset{\sim}{G}(\eta, 2\omega) \cdot \underset{\approx}{\chi}(q, 2\omega; q_1, \omega) : \underset{\sim}{E}^{(0)}(q_1, \omega) \underset{\sim}{E}^{(0)}(q - q_1, \omega)$$

$$\times 16\pi(\omega/c)^2 \exp i(\eta(z - z') + qz'). \tag{72}$$

The Green's function tensor is given by its inverse, equation (65), for this case

$$[\underset{\sim}{G}(\eta, \omega)]^{-1} = \begin{bmatrix} \eta^2 - (\omega/c)^2 \epsilon_{xx} & -(\omega/c)^2 \epsilon_{xy} & -(\omega/c)^2 \epsilon_{xz} \\ -(\omega/c)^2 \epsilon_{yx} & \eta^2 - (\omega/c)^2 \epsilon_{yy} & -(\omega/c)^2 \epsilon_{yz} \\ -(\omega/c)^2 \epsilon_{zx} & -(\omega/c)^2 \epsilon_{zy} & -(\omega/c)^2 \epsilon_{zz} \end{bmatrix}. \tag{73}$$

In principle the dielectric tensor, $\underset{\sim}{\epsilon}$, and the nonlinear susceptibility, $\underset{\approx}{\chi}$, may be calculated according to the results in Section V. However a lack of knowledge of the unperturbed states of the crystal makes a complete solution impossible. We can apply overall symmetry relations, though, which considerably simplify these tensors. In the long wavelength limit, KDP, which has tetragonal scalenohedral symmetry (D_{2d}), has but two independent components for either $\underset{\sim}{\epsilon}$ or $\underset{\approx}{\chi}$ in the crystal coordinate system. These are given in Appendix C together with the transformations to the coordinate system which we are using in this problem. For the optical conditions this symmetry is effectively reduced, but the long wavelength case represents an upper bound on the symmetry and yields all the physical properties of interest.

In Appendix D we compute the Green's function tensor from its inverse (73). There are singularities in $\underset{\sim}{G}(\eta, \omega)$ when η is a wavevector that satisfies the homogeneous equation (67) for a particular frequency. The resulting relations of the phase velocity to the dielectric tensor components and propagation direction at these singularities are known as Fresnel's equations. The Green's function thus yields information about the fields in a linear, anisotropic medium as well as in the nonlinear domain.

We now make use of the nonlinear susceptibility tensor in our frame, given in Appendix C, and $\underset{\sim}{G}(\eta, \omega)$, given in equation (D6), to put (71) and (72) in full component form. For notational brevity we define $\chi_o = \chi_1 \sin\varphi_o \cos\varphi_o \sin\psi_o$ and $\epsilon_o = \epsilon_1 \sin^2\psi_o + \epsilon_2 \cos^2\psi_o$. Thus we generate the following first order field components,

$$E_y^{(1)}(q, \omega) \exp iqz - E_y^{(0)}(q, \omega) \exp iq_1 z$$

$$= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\eta \int dz' \, 4\pi(\omega/c)^2 \exp i(\eta(z-z') + qz')(\eta^2 - q_1^2)^{-1}$$

$$\times E_y^{(0)*}(q_2-q, \omega) [4\chi_o E_x^{(0)}(q_2, 2\omega) + 4\chi_o \cot\psi_o \, E_z^{(0)}(q_2, 2\omega)], \qquad (74)$$

$$E_x^{(1)}(q, 2\omega) \exp iqz - E_x^{(0)}(q_2, 2\omega) \exp iq_2 z$$

$$= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\eta \int dz' \, 16\pi(\omega/c)^2 \exp i(\eta(z-z') + qz')(\eta^2 - q_2^2)^{-1}$$

$$\times E_y^{(0)}(q_1, \omega) E_y^{(0)}(q-q_1, \omega) [2\chi_o + 2\chi_o\chi_2 \cos^2 \psi_o(\epsilon_2 - \epsilon_1)/\epsilon_o\chi_1], \qquad (75)$$

$$E_z^{(1)}(q, 2\omega) \exp iqz - E_z^{(0)}(q_2, 2\omega) \exp iq_2 z$$

$$= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\eta \int dz' \, 16\pi(\omega/c)^2 \exp i(\eta(z-z') + qz')(\eta^2 - q_2^2)^{-1}$$

$$\times E_y^{(0)}(q_1, \omega) E_y^{(0)}(q-q_1, \omega) [2\chi_o(\epsilon_2 - \epsilon_1) \sin \psi_o \cos \psi_o/\epsilon_o$$

$$+ 2\chi_o\chi_2 \cot \psi_o(\eta^2(c/\omega)^2 - \epsilon_1 - \epsilon_2 + \epsilon_o)/\epsilon_o] \, . \qquad (76)$$

In each of these equations the integral over $d\eta$ has a singularity whenever $\eta = \pm q_{1,2}$. If we want to examine the waves at $z > \ell$, that is, the transmitted waves, during the whole of the integration of dz' from $0 \le z' \le \ell$ we have $z - z' > 0$. For this case the integral may be computed along a closed contour in the complex η plane along the real axis and an infinite semicircle in the upper half plane. Figure 2 gives the appropriate contour. The way we encircle the poles is a statement of the boundary conditions. We assume that to the right of the crystal only waves traveling to the right are present; so the correct pole to enclose is $\eta = +q_{1,2}$. This presumes that the incident waves are all coming from the left. Integrating out the $d\eta$ over this contour in the latter three equations, we obtain in each case the factor $2\pi i \times$ Residue at $\eta = +q_{1,2}$. This leaves only the integral defined by

$$I_\ell = \int_0^\ell dz' \exp i(q - q_{1,2})z' = \left(2 \exp\left(i(q-q_{1,2})\ell/2\right)\right)$$

$$\times \left(\sin\left((q-q_{1,2})\ell/2\right)\right) \Big/ (q-q_{1,2}) \, . \qquad (77)$$

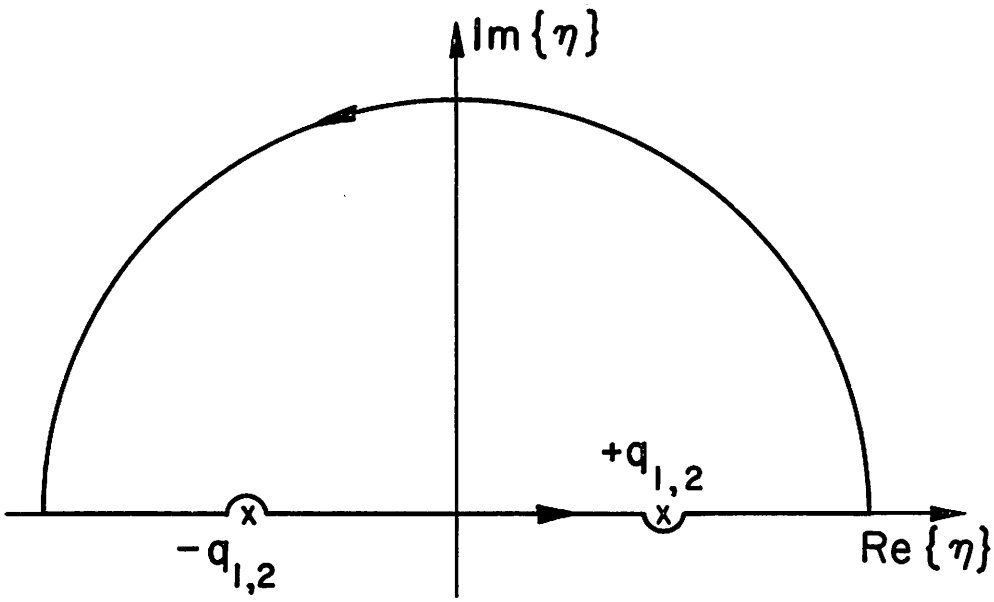

Fig. 2. Contour of integration.

This integral is known as the coherence integral in the theory of traveling wave parametric amplifiers.

The coherence integral indicates the importance of conservation of wavevector for the nonlinear interaction. Since $\ell >> (q_{1,2})^{-1}$ the integral practically vanishes for all q except $q \cong q_{1,2}$. For perfect matching, a condition called "synchronism," we have $q = q_{1,2}$ and $I_\ell = \ell$. In order that this condition be met, we must have $E_y^{(0)}(q_2 - q_1, \omega)$ as a possible zeroth order wave in the crystal since this term appears in the integrals (74) - (76). We interpret this condition diagrammatically in Figure 3 where we draw the solutions to Fresnel's equations in wavevector space on the isofrequency surfaces ω and 2ω.

Clearly the line $\overline{BC}$ must equal $\overline{AB}$ if we confine ourselves to collinear propagation so that $2q_1 = q_2$. This may alternatively be stated that the phase velocity of the 2ω wave is equal to the phase velocity of the ω wave. In terms of the Fresnel equations and notation in Appendix D, we see that

$$v_{p_1}^2(\omega) \equiv (\omega/q_1)^2 = v_o^2(\omega) \tag{78}$$

$$v_{p_2}^2(2\omega) \equiv (2\omega/q_2)^2 = v_o^2(2\omega)\cos^2\psi_o + v_e^2(2\omega)\sin^2\psi_o \tag{79}$$

are equal when

$$\psi_o = \arcsin\left[\left(v_o^2(\omega) - v_o^2(2\omega)\right)\Big/\left(v_e^2(2\omega) - v_o^2(2\omega)\right)\right]^{1/2} . \tag{80}$$

Here v_o and v_e are the ordinary and extraordinary velocities defined by $v_o = c(\epsilon_1)^{-1/2}$ and $v_e = c(\epsilon_2)^{-1/2}$. Equation (80) has been given by Giordmaine[11]; it has a real solution when the square rooted quantity is between zero and one. Thus the anisotropy at 2ω, $(v_e^2(2\omega) - v_o^2(2\omega))$ must be greater than the dispersion between the two frequencies $(v_o^2(\omega) - v_o^2(2\omega))$. KDP is such a crystal and, for the values of v_o and v_e given in (D7), we obtain the phase matching angle $\psi_o \cong 50^o$.

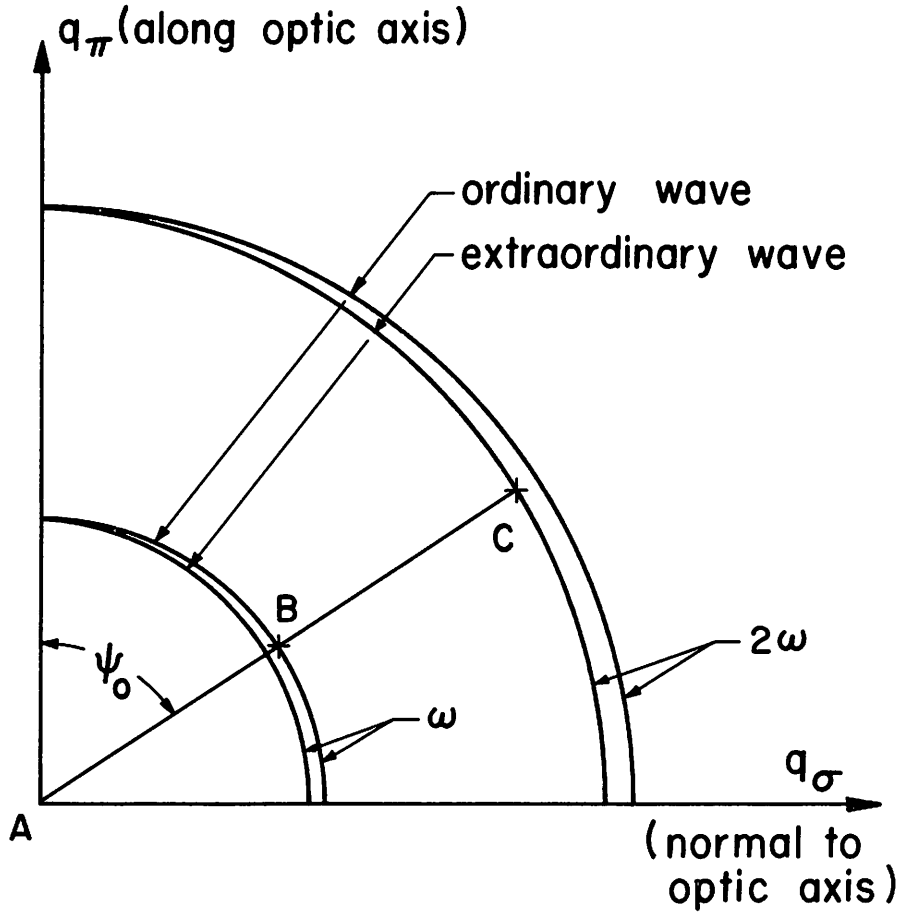

Fig. 3. Fresnel equation solutions in negative uniaxial crystals.

We may evaluate the fields (74) - (76) by means of the contour integration and the coherence integral. For the purposes of numerical calculation, we take the phase matching condition, $I_\ell = \ell$, to hold and neglect terms of the order of the crystal anisotropy, $(\epsilon_2 - \epsilon_1)/\epsilon_o \approx 3\%$. To the same order we may neglect the nontransverse field $E_z(q_2, 2\omega)$ since it is proportional to $\sin\alpha$ which in turn is proportional to $(\epsilon_2 - \epsilon_1)/\epsilon_o$. Equations (74) and (75) then give

$$E_y^{(1)}(q_1, \omega) - E_y^{(0)}(q_1, \omega) \cong E_y^{(0)*}(q_1, \omega) E_x^{(0)}(q_2, 2\omega)$$

$$\times (8\pi\, i\ell\omega^2/c^2 q_1)\, \chi_1(q_1, \omega; q_2, 2\omega) \sin\varphi_o \cos\varphi_o \sin\psi_o, \qquad (81)$$

$$E_x^{(1)}(q_2, 2\omega) - E_x^{(0)}(q_2, 2\omega) \cong E_y^{(0)}(q_1, \omega) E_y^{(0)}(q_1, \omega)$$

$$\times (16\pi\, i\ell\omega^2/c^2 q_2)\, \chi_1(q_2, 2\omega; q_1, \omega) \sin\varphi_o \cos\varphi_o \sin\psi_o. \qquad (82)$$

We have restored the definition of χ_o and added the frequency and wave-vector dependent argument for χ_1 which we dropped explicitly in Appendix C because of our static approximation.

$\sin\psi_o$ has been fixed by the synchronism condition (80) but we may still maximize the interaction by setting $\varphi_o = 45^o$. Maker et al[12] demonstrate the validity of the angular dependence in (82) for harmonic generation in KDP. Returning to the definition of χ_o and ignoring any dispersion in the nonlinear susceptibility, we introduce two gain parameters - $T_{\omega\to 2\omega}$ for harmonic generation and its reverse $T_{2\omega\to\omega}$ for subharmonic generation. From equations (82) and (81) then, we define

$$T_{\omega\to 2\omega} = \left(E_x^{(1)}(q_2, 2\omega) - E_x^{(0)}(q_2, 2\omega)\right) \Big/ \left(E_y^{(0)}(q_1, \omega)\right)$$

$$= (16\pi\, i\, \ell\omega^2/c^2 q_2)\, \chi_o\, E_y^{(0)}(q_1, \omega), \qquad (83)$$

$$T_{2\omega\to\omega} = \left(E_y^{(1)}(q_1, \omega) - E_y^{(0)}(q_1, \omega)\right) \Big/ \left(E_y^{(0)*}(q_1, \omega)\right)$$

$$= (8\pi\, i\ell\omega^2/c^2 q_1)\, \chi_o\, E_x^{(0)}(q_2, 2\omega)\,. \qquad (84)$$

Let us assume that the first order waves are in phase with the zeroth order waves; this is the condition of maximum conversion efficiency. With θ_1 the phase of the wave at frequency ω and θ_2 at 2ω, we see from (82) that $2\theta_1 - \theta_2 + (\pi/2) = 0$ or integer multiples of 2π (assuming χ_o to be real) and similarly from (81) we have that $2\theta_1 - \theta_2 - (\pi/2) = 0$ or integer multiples of 2π. These phase conditions determine which way the nonlinear frequency conversion will proceed. Such phase relations are well known in the coupled mode theory of parametric amplifiers (e.g., Louisell,[13] Chapter 4).

Suppose now we have only a single wave incident on the crystal at frequency ω, and we start to generate the 2ω field with the proper phase as just discussed. The power generated in the 2ω wave divided by the incident power at ω is given by

$$P_{out}(2\omega)/P_{in}(\omega) = |T_{\omega\to 2\omega}|^2$$

$$= (16\pi\chi_o \ell\omega^2/c^2 q_2)\, |E_y^{(0)}(q_1, \omega)|^2\,. \qquad (85)$$

This power ratio thus depends on the "coherence length" ℓ of the crystal and the magnitude of the incident radiation. We designate ℓ as the coherence length now to remind us that we have matched phase velocities throughout the medium. In practice it is difficult to have synchronism throughout the crystal because of lattice inhomogeneities and incoherence of the light source. Maker et al[12] were able to achieve power conversion ratios of $> 10^{-6}$ with ruby laser light reasonably matched in a 1.5 mm plate of KDP.

Suppose now that the incident wave at ω is intended to produce the subharmonic $\omega/2$. According to equation (81), if $E_y^{(0)*}(q_1, \omega/2)$ were absent, there would be no such conversion. Therefore we must artificially introduce a small amount of subharmonic to start the process; we could externally supply it or rely on the noise level. This triggering process is fundamental to all down-conversion problems, but in the optical range the noise level is low at normal temperatures, reducing the reliability of starting such a device. However, assuming that the subharmonic is present to some degree and that the phases are optimized, the quantity $|T_{\omega\to\omega/2}|$ gives the first order gain per pass of the subharmonic wave amplitude. From (84) we see $|T_{\omega\to\omega/2}| = (2\pi\ell\omega^2/c^2 q_1)\chi_o |E_x^{(0)}(q_2, \omega)|$; so since q_1 of the subharmonic problem is $q_2/4$ of the harmonic case and if we have equal incident powers, $|E_x^{(0)}(q_2, \omega)|_{\text{Subharmonic case}} = |E_y^{(0)}(q_1, \omega)|_{\text{Harmonic case}}$, we see that $|T_{\omega\to\omega/2}|$ is equivalent to the previously calculated $|T_{\omega\to 2\omega}|/2$. Taking the experimental harmonic conversion ratio to be $\sim 10^{-6}$ we find that the amplitude gain per pass should then be $\sim 0.5 \times 10^{-3}$. This would be a power gain per pass of $\sim 10^{-3}$.

This minute gain per pass could be increased in a regenerative amplifier scheme, such as using mirrors to increase the number of passes. The mirrors need have losses of less than 0.1% both in reflection and diffraction. This is quite a critical requirement, but with increased fluxes available and better matching techniques, subharmonic optical generation should become possible. Kingston[14] has proposed this device in a short communication.

APPENDIX A

We wish to show that the complex current density, as defined in equation (9), is gauge invariant to infinitesimal gauge transformations. Thus we need only to show that the part linear in the fields is so invariant. It is first necessary to generalize the gauge to include a scalar potential, $ev(\underset{\sim}{x}, t)$, in the perturbation energy, $V(\underset{\sim}{x}, t)$, of equation (2). Rederiving the Fourier transform of the linear current density, we see that we must add $(\underset{\sim}{k} + \underset{\sim}{q}\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}}(-mc)v(\underset{\sim}{q}, \underset{\sim}{G}', \omega) | \underset{\sim}{k}\gamma)$ to the last matrix element in equation (13) in the general gauge. Here $v(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ is the expansion coefficient of the Fourier analyzed scalar potential.

A gauge transformation characterized by the scalar function $\psi(\underset{\sim}{x}, t)$ such that $\underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \longrightarrow \underset{\sim}{A}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) + (\underset{\sim}{q} + \underset{\sim}{G})\psi(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ and $v(\underset{\sim}{q}, \underset{\sim}{G}, \omega) \longrightarrow v(\underset{\sim}{q}, \underset{\sim}{G}, \omega) + (\omega/c)\psi(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ is performed on the current density. The portion of $\underset{\sim}{j}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ that depends on ψ is written

$$\underset{\sim}{j}_1^{(\psi)}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(e^2/mc\Omega)\sum_{\underset{\sim}{k}\gamma\underset{\sim}{G}'} \Bigg[f_o(\epsilon_{\underset{\sim}{k}\gamma})(\underset{\sim}{q}+\underset{\sim}{G}')(\underset{\sim}{k}\gamma | e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}} | \underset{\sim}{k}\gamma)\psi(\underset{\sim}{q}, \underset{\sim}{G}', \omega)$$

$$+ \sum_{\gamma'} \left(F^{\underset{\sim}{q}}_{\gamma'\gamma, \omega} / m \right) (\underset{\sim}{k}\gamma | \left(\underset{\sim}{p} + \hbar \left(\underset{\sim}{k} + (\underset{\sim}{q} + \underset{\sim}{G})/2 \right) \right) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} | \underset{\sim}{k} + \underset{\sim}{q}\gamma')$$

$$\times (\underset{\sim}{k}+\underset{\sim}{q}\gamma' | e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} \left((\underset{\sim}{q}+\underset{\sim}{G}')\cdot \left(\underset{\sim}{p}+\hbar\left(\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{G}')/2 \right) \right) - m\omega \right) | \underset{\sim}{k}\gamma)\psi(\underset{\sim}{q}, \underset{\sim}{G}', \omega) \Bigg] . \quad \text{(A1)}$$

It is an elementary result of $\underset{\sim}{k}\cdot\underset{\sim}{p}$ perturbation theory that

$$(\underset{\sim}{k} + \underset{\sim}{q}\gamma' | \ e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} (\underset{\sim}{q} + \underset{\sim}{G}')\cdot \left(\underset{\sim}{p} + \hbar\left(\underset{\sim}{k} + (\underset{\sim}{q} + \underset{\sim}{G}')/2 \right) \right) | \underset{\sim}{k}\gamma)$$

$$= (m/\hbar)(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'} - \epsilon_{\underset{\sim}{k}\gamma})(\underset{\sim}{k} + \underset{\sim}{q}\gamma' | \ e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}} | \underset{\sim}{k}\gamma). \quad \text{(A2)}$$

Inserting this into $\underset{\sim}{j}_1^{(\psi)}(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$, we obtain

$$\underset{\sim}{j}_1^{(\psi)}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(e^2/mc\Omega)\sum_{\underset{\sim}{G}'}\psi(\underset{\sim}{q}, \underset{\sim}{G}', \omega)\left\{\sum_{\underset{\sim}{k}\gamma\gamma'}[f_o(\epsilon_{\underset{\sim}{k}\gamma})\delta_{\gamma\gamma'}\right.$$

$$\times(\underset{\sim}{q}+\underset{\sim}{G}')(\underset{\sim}{k}\gamma|e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)] + \left[\left(\left(f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'}) - f_o(\epsilon_{\underset{\sim}{k}\gamma})\right)/\hbar\right)\right.$$

$$\left.\left.\times(\underset{\sim}{k}\gamma|\left(\underset{\sim}{p}+\hbar\left(\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{G})/2\right)\right)e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}}|\underset{\sim}{k}+\underset{\sim}{q}\gamma)(\underset{\sim}{k}+\underset{\sim}{q}\gamma'|e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)\right]\right\}. \quad (A3)$$

Now we exchange dummy indices $\gamma \leftrightarrow \gamma'$ and $\underset{\sim}{k}+\underset{\sim}{q} \leftrightarrow -\underset{\sim}{k}$ under the summation for the $f_o(\epsilon_{\underset{\sim}{k}+\underset{\sim}{q}\gamma'})$ term, and we note that $f_o(\epsilon_{-\underset{\sim}{k}\gamma}) = f_o(\epsilon_{\underset{\sim}{k}\gamma})$ and $|\underset{\sim}{k}\gamma) = |-\underset{\sim}{k}\gamma)^*$ when the Hamiltonian is invariant under time reversal and independent of spin. This allows us to write

$$\underset{\sim}{j}_1^{(\psi)}(\underset{\sim}{q}, \underset{\sim}{G}, \omega) = -(e^2/mc\Omega)\sum_{\underset{\sim}{G}'}\psi(\underset{\sim}{q}, \underset{\sim}{G}', \omega)\left\{\sum_{\underset{\sim}{k}\gamma\gamma'}[f_o(\epsilon_{\underset{\sim}{k}\gamma})\delta_{\gamma\gamma'}\right.$$

$$\times(\underset{\sim}{q}+\underset{\sim}{G}')(\underset{\sim}{k}\gamma|e^{-i(\underset{\sim}{G}\cdot\underset{\sim}{G}')\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)] - \left[\left(2f_o(\epsilon_{\underset{\sim}{k}\gamma})/\hbar\right)\right.$$

$$\left.\left.\times(\underset{\sim}{k}\gamma|\left(\underset{\sim}{p}+\hbar(\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{G})/2)\right)e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}}|\underset{\sim}{k}+\underset{\sim}{q}\gamma')(\underset{\sim}{k}+\underset{\sim}{q}\gamma'|e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)\right]\right\}$$

$$= -(e^2/mc\Omega)\sum_{\underset{\sim}{k}\gamma\underset{\sim}{G}'}\psi(\underset{\sim}{q}, \underset{\sim}{G}', \omega)\left\{f_o(\epsilon_{\underset{\sim}{k}\gamma})(\underset{\sim}{q}+\underset{\sim}{G}')(\underset{\sim}{k}\gamma|e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)\right.$$

$$\left.-\left(2f_o(\epsilon_{\underset{\sim}{k}\gamma})/\hbar\right)(\underset{\sim}{k}\gamma|\left(\underset{\sim}{p}+\hbar(\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{G})/2)\right)e^{-i(\underset{\sim}{G}-\underset{\sim}{G}')\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)\right\}$$

$$= 0. \quad (A4)$$

In the next to last step we have used the completeness relation $\sum_{\gamma'}|\underset{\sim}{k}\gamma')(\underset{\sim}{k}\gamma'| = 1$, and finally we take advantage of the oddness of $(\underset{\sim}{k}\gamma|\left(\underset{\sim}{p}+\hbar(\underset{\sim}{k}-\underset{\sim}{G}'/2)\right)e^{i\underset{\sim}{G}'\cdot\underset{\sim}{x}}|\underset{\sim}{k}\gamma)$ under reversal of $\underset{\sim}{k}$.

Thus we see $\underset{\sim}{j}_1(\underset{\sim}{q}, \underset{\sim}{G}, \omega)$ is invariant under gauge transformation; so we choose a gauge such that $\dot{\psi} = icv$ to eliminate the scalar potential entirely from the equations in the text.

APPENDIX B

The equilibrium part of the complex current density given by (12) is seen to be

$$\underset{\sim}{j}_o(\underset{\sim}{q}, \underset{\sim}{G}) = (e/m\Omega) \sum_{\underset{\sim}{k}\gamma} (\underset{\sim}{k}\gamma \,|\, \left(\underset{\sim}{p}+\hbar(\underset{\sim}{k}+\underset{\sim}{G}/2)\right) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} |\, \underset{\sim}{k}\gamma)\, f_o(\epsilon_{\underset{\sim}{k}\gamma})\delta_{\underset{\sim}{q}0}, \qquad \text{(B1)}$$

since ρ_o is diagonal in the Bloch representation. Thus $\underset{\sim}{j}_o$ is periodic in the lattice as it has nonvanishing coefficients only when $\underset{\sim}{q} = 0$. In fact if H_o is invariant under time reversal, then, as in appendix A, $f_o(\epsilon_{\underset{\sim}{k}\gamma})$ is even and $(\underset{\sim}{k}\gamma \,|\, \left(\underset{\sim}{p}+\hbar(\underset{\sim}{k}+\underset{\sim}{G}/2)\right) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{x}} |\, \underset{\sim}{k}\gamma)$ is odd under reversal of $\underset{\sim}{k}$. In this widely applicable circumstance there is no equilibrium current.

APPENDIX C

We give in this appendix the dielectric and nonlinear susceptibility tensors for KDP.

KH_2PO_4 has tetragonal scalenohedral symmetry (Schoenflies D_{2d}(Vd), International $\bar{4}2$ m). The only second and third rank tensors compatible with this symmetry are (Mason,[15] Chapter 3)

$$\underset{\sim}{\epsilon}^{(c)} = \begin{bmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_1 & 0 \\ 0 & 0 & \epsilon_2 \end{bmatrix} \tag{C1}$$

and

$$\underset{\approx}{\chi}^{(c)} = \begin{bmatrix} 0 & 0 & 0 & \chi_1 & 0 & 0 & \chi_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \chi_1 & 0 & 0 & \chi_1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \chi_2 & 0 & 0 & \chi_2 \end{bmatrix} \tag{C2}$$

where we are in the crystallographic coordinate system. We must transform these tensors to the coordinate system illustrated in Figure 1. First we rotate about $z^{(c)}$ by $(\pi/2) - \varphi_o$ and then about y by ψ_o. The transformation of axes is

$$\underset{\sim}{x} = [+\psi_o]\,[(\pi/2) - \varphi_o]\,\underset{\sim}{x}^{(c)} \tag{C3}$$

where

$$[(\pi/2) - \varphi_o] = \begin{bmatrix} \sin\varphi_o & -\cos\varphi_o & 0 \\ \cos\varphi_o & \sin\varphi_o & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{C4}$$

and

$$[+\psi_o] = \begin{bmatrix} \cos\psi_o & 0 & -\sin\psi_o \\ 0 & 1 & 0 \\ \sin\psi_o & 0 & \cos\psi_o \end{bmatrix} \tag{C5}$$

Thus in the transformed coordinate system

$$\underset{\sim}{\epsilon} = [+\psi_o]\ [(\pi/2) - \varphi_o]\ \underset{\sim}{\epsilon}^{(c)}\ [-(\pi/2) + \varphi_o]\ [-\psi_o]$$

$$= \begin{bmatrix} \epsilon_1 \cos^2\psi_o + \epsilon_2 \sin^2\psi_o & 0 & (\epsilon_2 - \epsilon_1) \sin\psi_o \cos\psi_o \\ 0 & \epsilon_1 & 0 \\ (\epsilon_2 - \epsilon)\sin\psi_o \cos\psi_o & 0 & \epsilon_1 \cos^2\psi_o + \epsilon_2 \cos^2\psi_o \end{bmatrix}. \tag{C6}$$

To compute the components of $\underset{\approx}{\chi}$, we use the general tensor transformation law with the usual summation over repeated indices

$$\chi_{\lambda\mu\nu} = \frac{\partial x_\lambda}{\partial x_\rho^{(c)}} \frac{\partial x_\mu}{\partial x_\sigma^{(c)}} \frac{\partial x_\nu}{\partial x_\tau^{(c)}} \chi_{\rho\sigma\tau}^{(c)}. \tag{C7}$$

We obtain the differentials from (C3). The middle column is multiplied by χ_1 and the right hand column by χ_2.

	χ_1	χ_2
χ_{xxx}	$-4 \sin\varphi_o \cos\varphi_o \sin\psi_o \cos^2\psi_o$	$-2 \sin\varphi_o \cos\varphi_o \sin\psi_o \cos^2\psi_o$
χ_{xyy}	$2 \sin\varphi_o \cos\varphi_o \sin\psi_o$	0
χ_{xzz}	$2 \sin\varphi_o \cos\varphi_o (\sin\psi_o \cos^2\psi_o - \sin^3\psi_o)$	$2 \sin\varphi_o \cos\varphi_o \sin\psi_o \cos^2\psi_o$
$\chi_{xyz} = \chi_{xzy}$	$(\sin^2\varphi_o - \cos^2\varphi_o) \cos^2\psi_o$	$-(\sin^2\varphi_o - \cos^2\varphi_o) \sin^2\psi_o$
$\chi_{xxz} = \chi_{xzx}$	$2 \sin\varphi_o \cos\varphi_o (\sin^2\psi_o \cos^2\psi_o - \cos^3\psi_o)$	$2 \sin\varphi_o \cos\varphi_o \sin^2\psi_o \cos\psi_o$
$\chi_{xxy} = \chi_{xyx}$	$(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$	$(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$
χ_{yxx}	$2(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$	0
χ_{yyy}	0	0
χ_{yzz}	$-2(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$	0
$\chi_{yyz} = \chi_{yzy}$	$2 \sin\varphi_o \cos\varphi_o \cos\psi_o$	0
$\chi_{yxz} = \chi_{yzx}$	$-(\sin^2\varphi_o - \cos^2\varphi_o)(\sin^2\psi_o - \cos^2\psi_o)$	0
$\chi_{yxy} = \chi_{yyx}$	$2 \sin\varphi_o \cos\varphi_o \sin\psi_o$	0
χ_{zxx}	$4 \sin\varphi_o \cos\varphi_o \sin^2\psi_o \cos\psi_o$	$-2 \sin\varphi_o \cos\varphi_o \cos^3\psi_o$
χ_{zyy}	0	$2 \sin\varphi_o \cos\varphi_o \cos\psi_o$
χ_{zzz}	$-4 \sin\varphi_o \cos\varphi_o \sin^2\psi_o \cos\psi_o$	$-2 \sin\varphi_o \cos\varphi_o \sin^2\psi_o \cos\psi_o$
$\chi_{zyz} = \chi_{zzy}$	$-(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$	$-(\sin^2\varphi_o - \cos^2\varphi_o) \sin\psi_o \cos\psi_o$
$\chi_{zxz} = \chi_{zzx}$	$2 \sin\varphi_o \cos\varphi_o (\sin\psi_o \cos^2\psi_o - \sin^3\psi_o)$	$2 \sin\varphi_o \cos\varphi_o \sin\psi_o \cos^2\psi_o$
$\chi_{zxy} = \chi_{zyx}$	$-(\sin^2\varphi_o - \cos^2\varphi_o) \sin^2\psi_o$	$(\sin^2\varphi_o - \cos^2\varphi_o) \cos^2\psi_o$

(C8)

APPENDIX D

We would now like to compute the Fourier transform of the Green's function tensor. Its inverse is given in (73) and the dielectric tensor appears in (C6). We have

$$\underset{\sim}{G}(\eta, \omega)^{-1} = \frac{\omega^2}{c^2}\begin{bmatrix} (\eta c/\omega)^2-(\epsilon_1\cos^2\psi_o+\epsilon_2\sin^2\psi_o) & 0 & -(\epsilon_2-\epsilon_1)\sin\psi_o\cos\psi_o \\ 0 & (\eta c/\omega)^2-\epsilon_1 & 0 \\ -(\epsilon_2-\epsilon_1)\sin\psi_o\cos\psi_o & 0 & -(\epsilon_1\sin^2\psi_o+\epsilon_2\cos^2\psi_o) \end{bmatrix} \tag{D1}$$

The inverse of (D1) is

$$\left[\underset{\sim}{G}(\eta, \omega)\right]_{\mu\nu} = \left[\underset{\sim}{G}(\eta, \omega)^{-1}\right]^{\nu\mu} / \left|\underset{\sim}{G}(\eta, \omega)^{-1}\right| \tag{D2}$$

where the numerator is the signed cofactor and the denominator is the determinant. The determinant may be evaluated simply

$$\left|\underset{\sim}{G}(\eta, \omega)^{-1}\right| = -(\omega/c)^2(\epsilon_1\sin^2\psi_o + \epsilon_2\cos^2\psi_o)$$
$$\times \left((\eta c/\omega)^2-\epsilon_1\right)\left((\eta c/\omega)^2-\left(\epsilon_1\epsilon_2/(\epsilon_1\sin^2\psi_o+\epsilon_2\cos^2\psi_o)\right)\right) . \tag{D3}$$

The roots of this determinant have the important property that they are singularities in the Green's function integral (63). These poles enable us to evaluate that integral by contour integration in the complex η plane. The roots give precisely the Fresnel equations for light propagation in a uniaxial crystal, so the poles are found at wavevectors that are solutions to the homogeneous linear wave equation. We may immediately factor equation (D3) to obtain the two roots when $\eta = q_1$ or q_2 and

$$(\omega/q_1)^2 = v_{p_1}^2 = v_o^2 \qquad \text{[ordinary wave]} \tag{D4}$$

$$(\omega/q_2)^2 = v_{p_2}^2 = v_o^2\cos^2\psi_o + v_e^2\sin^2\psi_o \quad \text{[extraordinary wave]}. \tag{D5}$$

From Section X we restate three definitions: $v_o^2 = c^2/\epsilon_1$; $v_e^2 = c^2/\epsilon_2$; $\epsilon_o = \epsilon_1 \sin^2\psi_o + \epsilon_2 \cos^2\psi_o$. Then by performing the operations indicated in (D2), we find that the Green's function tensor is

$$\underset{\sim}{G}(\eta, \omega) = \begin{bmatrix} \dfrac{1}{(\eta^2 - q_2^2)} & 0 & \dfrac{(\epsilon_2-\epsilon_1)\sin\psi_o\cos\psi_o}{\epsilon_o(\eta^2 - q_2^2)} \\ 0 & \dfrac{1}{(\eta^2 - q_1^2)} & 0 \\ \dfrac{(\epsilon_2-\epsilon_1)\sin\psi_o\cos\psi_o}{\epsilon_o(\eta^2 - q_2^2)} & 0 & \dfrac{(\eta c/\omega)^2 - \epsilon_1 - \epsilon_2 + \epsilon_o}{\epsilon_o(\eta^2 - q_2^2)} \end{bmatrix} . \qquad \text{(D6)}$$

In general ϵ_1 and ϵ_2 are functions of frequency as are q_1 and q_2. For KDP at $\omega = 2.72 \times 10^{15}$ sec^{-1} and $2\omega = 5.44 \times 10^{15}$ sec^{-1} which corresponds to the fundamental and second harmonic ruby laser light (6943Å), we list the quantities as given by Giordmaine[11] for reference.

$$\sqrt{\epsilon_1(\omega)} = c/v_o(\omega) = 1.506$$

$$\sqrt{\epsilon_1(2\omega)} = c/v_o(2\omega) = 1.534$$

$$\sqrt{\epsilon_2(\omega)} = c/v_e(\omega) = 1.466$$

$$\sqrt{\epsilon_2(2\omega)} = c/v_e(2\omega) = 1.487 . \qquad \text{(D7)}$$

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