

## Quantum Theory of the Dielectric Constant in Real Solids

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(Received October 12, 1961)

The quantum theory of the frequency- and wave-number-dependent dielectric constant in solids is extended in order to study the full dielectric constant tensor and to include local-field effects. Within the framework of the band theory, an explicit expression for the dielectric constant tensor, neglecting local-field effects, is derived. In addition to components which are the ordinary longitudinal and transverse dielectric constants, there are components which couple transverse and longitudinal electromagnetic disturbances. A formalism for calculating the local-field corrections to the dielectric constant is developed in detail for the case of the longitudinal dielectric constant of a cubic insulating solid. In the coarsest (dipole) approximation, the theory gives a Lorenz-Lorentz formula modified by self-polarization corrections arising from the polarization of the charge in a unit cell by its own field.

QUANTUM mechanical treatments of the frequency- and wave-number-dependent dielectric constant in solids have been given by Nozières and Pines<sup>1</sup> and by Ehrenreich and Cohen.<sup>2</sup> These authors give explicit expressions for certain components of the dielectric constant tensor, valid within the framework of the random phase approximation (RPA). Expressions are not given for the remaining components of the dielectric constant tensor and local field effects are neglected. This paper will generalize the treatment of Ehrenreich and Cohen<sup>2</sup> so as to include additional effects of interest in real solids. In Sec. I an expression for the full frequency- and wave-number-dependent dielectric constant tensor in a solid of arbitrary symmetry will be derived, still neglecting local field effects. The additional components obtained correspond to a coupling between longitudinal and transverse electromagnetic disturbances. This coupling, which does not appear in an isotropic free electron gas, is present in solids of even cubic symmetry and vanishes only for propagation along special directions of high symmetry. In Sec. II, local field effects in insulators of cubic symmetry will be discussed. An integral equation will be set up which determines the longitudinal dielectric constant with local field corrections in the case of wavelengths large compared to the lattice constant but small compared to the over-all crystal dimensions. The integral equation will be rewritten by making a multipole expansion of the potential in a given cell arising from the charge density in all other cells. The solution, when only dipole terms are retained, is the modified Lorenz-Lorentz formula

$$\epsilon - 1 = \frac{4\pi(\alpha - C_1)}{1 - (4\pi/3)(\alpha - C_1)},$$

where  $\alpha$  is the polarizability of the solid calculated without making local field corrections, and  $C_1$  is a re-

duction in  $\alpha$  due to polarization of the charge in a given cell by its own field.

The calculations of Secs. I and II are performed within the framework of the one-electron (energy band) approximation and use a linearized Liouville equation to determine the single-particle density matrix. Since in this context linearization is equivalent to the RPA,<sup>2</sup> the results obtained in Secs. I and II are still valid only within the framework of the RPA.

### I. DIELECTRIC CONSTANT TENSOR

We will first introduce a phenomenological dielectric constant tensor. Let  $\mathbf{A}(\mathbf{r}, t)$  and  $\phi(\mathbf{r}, t)$  be the potentials describing fields acting on a system of charged particles. In response to the fields, charge and current densities  $\rho^{\text{ind}}(\mathbf{r}, t)$  and  $\mathbf{j}^{\text{ind}}(\mathbf{r}, t)$ , which satisfy the equation of continuity  $\nabla \cdot \mathbf{j}^{\text{ind}} + \partial \rho^{\text{ind}} / \partial t = 0$ , will be induced in the system. Let us immediately introduce Fourier transforms  $\mathbf{A}(\mathbf{q}, \omega)$ ,  $\phi(\mathbf{q}, \omega)$ ,  $\mathbf{j}^{\text{ind}}(\mathbf{q}, \omega)$ , etc., by

$$\mathbf{A}(\mathbf{r}, t) = \int d\mathbf{q} d\omega \mathbf{A}(\mathbf{q}, \omega) \exp(i\mathbf{q} \cdot \mathbf{r} - \omega t), \quad (1.1)$$

and similar equations.

In their treatments of the dielectric constant, Nozières and Pines<sup>1</sup> and Ehrenreich and Cohen,<sup>2</sup> following a practice originated by Lindhard,<sup>3</sup> define longitudinal and transverse dielectric constants  $\epsilon^L$  and  $\epsilon^T$  by the equations

$$-i\omega[\epsilon^{(L,T)}(\mathbf{q}, \omega) - \mathbf{1}] \cdot \mathbf{E}^{(L,T)}(\mathbf{q}, \omega) = 4\pi \mathbf{j}^{\text{ind}(L,T)}(\mathbf{q}, \omega). \quad (1.2)$$

The two constants describe respectively the longitudinal current induced by a purely-longitudinal electric field and the transverse current induced by a purely-transverse electric field. In the case of a free-electron gas a longitudinal (transverse) current cannot be induced by a transverse (longitudinal) electric field. Consequently  $\epsilon^L$  and  $\epsilon^T$  give a complete description of the linear dielectric properties. In solids, in general a

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<sup>1</sup> P. Nozières and D. Pines, *Phys. Rev.* **109**, 741, 762, 1062 (1958); *ibid.* **111**, 442 (1958); *ibid.* **113**, 1254 (1959).

<sup>2</sup> H. Ehrenreich and M. H. Cohen, *Phys. Rev.* **115**, 786 (1959).

<sup>3</sup> J. Lindhard, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **28**, 8 (1954).

purely-transverse or a purely-longitudinal electric field induces both transverse and longitudinal currents. In this case the linear dielectric properties are fully described by a dielectric-constant tensor defined by

$$-i\omega[\boldsymbol{\epsilon}(\mathbf{q},\omega)-\mathbf{1}]\cdot\mathbf{E}(\mathbf{q},\omega)=4\pi\mathbf{j}^{\text{ind}}(\mathbf{q},\omega). \quad (1.3)$$

The longitudinal and transverse constants  $\boldsymbol{\epsilon}^L(\mathbf{q},\omega)$  and  $\boldsymbol{\epsilon}^T(\mathbf{q},\omega)$  can be simply related to  $\boldsymbol{\epsilon}(\mathbf{q},\omega)$ . Let  $\hat{q}$  be a unit vector parallel to the direction of propagation  $\mathbf{q}$ , and define

$$\begin{aligned} \mathbf{1}_L &= \hat{q}\hat{q} \\ \mathbf{1}_T &= \mathbf{1} - \hat{q}\hat{q} \end{aligned} \quad (1.4)$$

where  $\mathbf{1}$  is the unit dyadic. Then letting  $\mathbf{E}(\mathbf{q},\omega)$  be purely longitudinal or purely transverse gives

$$\begin{aligned} \boldsymbol{\epsilon}^L(\mathbf{q},\omega) &= \mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q},\omega) \cdot \mathbf{1}_L, \\ \boldsymbol{\epsilon}^T(\mathbf{q},\omega) &= \mathbf{1}_T \cdot \boldsymbol{\epsilon}(\mathbf{q},\omega) \cdot \mathbf{1}_T. \end{aligned} \quad (1.5)$$

The remaining components of the dielectric-constant tensor are  $\mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q},\omega) \cdot \mathbf{1}_T$  and  $\mathbf{1}_T \cdot \boldsymbol{\epsilon}(\mathbf{q},\omega) \cdot \mathbf{1}_L$ , which vanish for a free-electron gas but do not in general vanish for a solid. They describe, respectively, the longitudinal (transverse) current induced by a transverse (longitudinal) electric field.

An explicit expression for  $\boldsymbol{\epsilon}(\mathbf{q},\omega)$  will be calculated in the energy-band approximation. Consider the single-particle Liouville equation

$$i\hbar\partial\rho/\partial t = [H, \rho], \quad (1.6)$$

where  $\rho$  is the single-particle density matrix and

$$H = (1/2m)[\mathbf{p} - (e/c)\mathbf{A}(\mathbf{r},t)]^2 + e\phi(\mathbf{r},t) + U(\mathbf{r}). \quad (1.7)$$

Here  $U(\mathbf{r})$  is the periodic lattice potential. Let the state functions for the unperturbed lattice be  $|\mathbf{k}l\rangle = V^{-1/2}u_{\mathbf{k}l} \times \exp(i\mathbf{k}\cdot\mathbf{r})$  with  $u_{\mathbf{k}l}$  cell-periodic and  $V$  the volume of the crystal. They satisfy the Schrödinger equation  $[\mathbf{p}^2/2m + U(\mathbf{r})]|\mathbf{k}l\rangle = E_{\mathbf{k}l}|\mathbf{k}l\rangle$ , in which  $\mathbf{k}$  is the wave vector and  $l$  the band index. Linearize the Liouville

$$\langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle = \frac{[f_0(E_{l\mathbf{k}}) - f_0(E_{l'\mathbf{k}+\mathbf{q}})]\langle l'\mathbf{k}+\mathbf{q}|l\mathbf{k}\rangle e\phi(\mathbf{q},\omega) - \langle l'\mathbf{k}+\mathbf{q}|\mathbf{p}_e + \hbar\mathbf{k} + \hbar\mathbf{q}/2|l\mathbf{k}\rangle \cdot (e/mc)\mathbf{A}(\mathbf{q},\omega)}{\hbar\omega + E_{l\mathbf{k}} - E_{l'\mathbf{k}+\mathbf{q}}}. \quad (1.13)$$

The induced current and charge density may be calculated from

$$\begin{aligned} \mathbf{j}^{\text{ind}}(\mathbf{r},t) &= \text{Tr}\rho^{(1)}\mathbf{j}_{\text{op}}^{(0)}(\mathbf{r}) + \text{Tr}\rho^{(0)}\mathbf{j}_{\text{op}}^{(1)}(\mathbf{r},t), \\ \rho^{\text{ind}}(\mathbf{r},t) &= \text{Tr}\rho^{(1)}\rho_{\text{op}}^{(0)}(\mathbf{r}), \end{aligned} \quad (1.14)$$

where

$$\begin{aligned} \mathbf{j}_{\text{op}}^{(0)}(\mathbf{r}) &= (\hbar/2m)[(\mathbf{p}_e/m)\delta(\mathbf{r}-\mathbf{r}_e) + \delta(\mathbf{r}-\mathbf{r}_e)(\mathbf{p}_e/m)], \\ \mathbf{j}_{\text{op}}^{(1)}(\mathbf{r}) &= -(e/mc)\mathbf{A}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}_e), \\ \rho_{\text{op}}^{(0)}(\mathbf{r}) &= e\delta(\mathbf{r}-\mathbf{r}_e), \end{aligned} \quad (1.15)$$

and  $\mathbf{r}_e$  and  $\mathbf{p}_e$  are, respectively, the position and mo-

mentum operators. This gives

$$\begin{aligned} i\hbar\partial\langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle/\partial t &= (E_{l'\mathbf{k}+\mathbf{q}} - E_{l\mathbf{k}})\langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle \\ &+ [f_0(E_{l\mathbf{k}}) - f_0(E_{l'\mathbf{k}+\mathbf{q}})] \\ &\times \langle l'\mathbf{k}+\mathbf{q}|\mathbf{p}_e + \hbar\mathbf{k} + \hbar\mathbf{q}/2|l\mathbf{k}\rangle \cdot \mathbf{A}(\mathbf{q},\omega). \end{aligned} \quad (1.8)$$

Let us assume

$$\begin{aligned} \mathbf{A}(\mathbf{r},t) &= \mathbf{A}(\mathbf{q},\omega) \exp i(\mathbf{q}\cdot\mathbf{r} - \omega t), \\ \phi(\mathbf{r},t) &= \phi(\mathbf{q},\omega) \exp i(\mathbf{q}\cdot\mathbf{r} - \omega t), \end{aligned} \quad (1.9)$$

and make the Ansatz that the time dependence of  $\langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle$  is  $\exp(-i\omega t)$ . The frequency  $\omega$  is taken to have a small positive imaginary part, corresponding to an adiabatic turning on of the perturbing potentials. It is an easy calculation to show that

$$\langle l'\mathbf{k}+\mathbf{q}'|e\phi|l\mathbf{k}\rangle = \delta_{\mathbf{q}',\mathbf{q}} e\phi(\mathbf{q},\omega) \langle l'\mathbf{k}+\mathbf{q}|l\mathbf{k}\rangle \quad (1.10)$$

and

$$\begin{aligned} \frac{1}{2}\langle l'\mathbf{k}+\mathbf{q}'|\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}|l\mathbf{k}\rangle &= \delta_{\mathbf{q}',\mathbf{q}} \langle l'\mathbf{k}+\mathbf{q}|\mathbf{p}_e + \hbar\mathbf{k} + \hbar\mathbf{q}/2|l\mathbf{k}\rangle \cdot \mathbf{A}(\mathbf{q},\omega). \end{aligned} \quad (1.11)$$

The abbreviation

$$\begin{aligned} \langle l'\mathbf{k}+\mathbf{q}|f(\mathbf{r}_e, \mathbf{p}_e)|l\mathbf{k}\rangle &\equiv (1/v_a) \int_0^1 u_{l'\mathbf{k}+\mathbf{q}}^*(\mathbf{r}) f(\mathbf{r}, -i\hbar\nabla_{\mathbf{r}}) u_{l\mathbf{k}}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (1.12)$$

has been introduced, in which the integration extends over a unit cell. Couplings of the wave vector  $\mathbf{q}$  to wave vectors  $\mathbf{q}+\mathbf{K}$ , where  $\mathbf{K}$  is a reciprocal lattice vector, have been neglected. These so-called Umklapp processes give rise to the local field corrections and will be discussed in Sec. II. The solution of Eq. (1.8) is immediately obtained in the form

mentum operators. This gives

$$\begin{aligned} \mathbf{j}^{\text{ind}}(\mathbf{q},\omega) &= -e^2\mathbf{A}(\mathbf{q},\omega)N/mcV \\ &+ \sum_{l\mathbf{k}} \langle l\mathbf{k}|\mathbf{p}_e + \hbar\mathbf{k} + \hbar\mathbf{q}/2|l'\mathbf{k}+\mathbf{q}\rangle \\ &\times \langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle, \end{aligned} \quad (1.16)$$

$$\begin{aligned} \rho^{\text{ind}}(\mathbf{q},\omega) &= (e/V) \sum_{l\mathbf{k}} \langle l\mathbf{k}|l'\mathbf{k}+\mathbf{q}\rangle \\ &\times \langle l'\mathbf{k}+\mathbf{q}|\rho^{(1)}|l\mathbf{k}\rangle, \end{aligned} \quad (1.17)$$

with  $N$  the number of cells in the crystal.

Since  $\mathbf{j}^{\text{ind}}(\mathbf{q},\omega)$  and  $\rho^{\text{ind}}(\mathbf{q},\omega)$  are obtained by linearization of a gauge-invariant theory with respect to the potentials, they are invariant under infinitesimal gauge transformations, and thus also under arbitrary gauge

transformations. This is verified explicitly, in the case of the expression for  $\mathbf{j}^{\text{ind}}(\mathbf{q}, \omega)$ , in the Appendix. Since the theory is gauge invariant, we may transform to a

gauge in which  $\phi=0$  without loss of generality. Note that  $\mathbf{A}$  will not in general be transverse in this gauge. From Eqs. (1.13) and (1.16) we get

$$\mathbf{j}^{\text{ind}}(\mathbf{q}, \omega) = -e^2 \mathbf{A}(\mathbf{q}, \omega) N / mcV$$

$$- \frac{e^2}{m^2 c V} \sum_{l' \mathbf{k}} \frac{(\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | l' \mathbf{k} + \mathbf{q}) [f_0(E_{l \mathbf{k}}) - f_0(E_{l' \mathbf{k} + \mathbf{q}})] (l' \mathbf{k} + \mathbf{q} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | \mathbf{l} \mathbf{k}) \cdot \mathbf{A}(\mathbf{q}, \omega)}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}}. \quad (1.18)$$

Comparing with Eq. (1.3) and noting that  $\mathbf{E}(\mathbf{q}, \omega) = i\omega \mathbf{A}(\mathbf{q}, \omega) / c$  gives

$$\boldsymbol{\epsilon}(\mathbf{q}, \omega) = (1 - 4\pi e^2 N / m V \omega^2) \mathbf{1}$$

$$+ \frac{4\pi e^2}{m^2 V \omega^2} \sum_{l' \mathbf{k}} \frac{(\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | l' \mathbf{k} + \mathbf{q}) [f_0(E_{l' \mathbf{k} + \mathbf{q}}) - f_0(E_{l \mathbf{k}})] (l' \mathbf{k} + \mathbf{q} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | \mathbf{l} \mathbf{k})}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}}, \quad (1.19)$$

an explicit expression for the frequency- and wave-number-dependent dielectric constant tensor.

It is interesting to compute  $\boldsymbol{\epsilon}^L(\mathbf{q}, \omega) = \mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_L$  directly from (1.19). This can be done by using the three identities

$$\mathbf{q} \cdot (\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | l' \mathbf{k} + \mathbf{q})$$

$$= (m / \hbar) (E_{l' \mathbf{k} + \mathbf{q}} - E_{l \mathbf{k}}) (\mathbf{l} \mathbf{k} | l' \mathbf{k} + \mathbf{q}), \quad (1.20)$$

$$0 = -N + (1 / \hbar q^2) \sum_{l' \mathbf{k}} \mathbf{q} \cdot (\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | l' \mathbf{k} + \mathbf{q})$$

$$\times [f_0(E_{l \mathbf{k}}) - f_0(E_{l' \mathbf{k} + \mathbf{q}})] (l' \mathbf{k} + \mathbf{q} | \mathbf{l} \mathbf{k}), \quad (1.21)$$

$$\mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_L = \mathbf{1}_L \left\{ 1 - 4\pi e^2 N / m V \omega^2 + \frac{4\pi e^2}{\hbar q^2 m V \omega^2} \sum_{l' \mathbf{k}} \mathbf{q} \cdot (\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q} / 2 | l' \mathbf{k} + \mathbf{q}) \right.$$

$$\left. \times [f_0(E_{l' \mathbf{k} + \mathbf{q}}) - f_0(E_{l \mathbf{k}})] (l' \mathbf{k} + \mathbf{q} | \mathbf{l} \mathbf{k}) \left( \frac{\hbar \omega}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}} - 1 \right) \right\}$$

$$= \mathbf{1}_L \left\{ 1 + \frac{4\pi e^2}{q^2 V} \sum_{l' \mathbf{k}} \frac{(\mathbf{l} \mathbf{k} | l' \mathbf{k} + \mathbf{q})^2 [f_0(E_{l' \mathbf{k} + \mathbf{q}}) - f_0(E_{l \mathbf{k}})]}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}} \right\}. \quad (1.23)$$

Equation (1.23) is just the longitudinal dielectric constant derived by Ehrenreich and Cohen.<sup>2</sup> Using the same identities employed to derive (1.23), it is easy to show that  $\mathbf{1}_T \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_L$  and  $\mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_T$  are given by

$$\mathbf{1}_T \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_L = \frac{4\pi e^2}{\omega q m V} \sum_{l' \mathbf{k}} \frac{\mathbf{1}_T \cdot (\mathbf{l} \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} | l' \mathbf{k} + \mathbf{q}) (l' \mathbf{k} + \mathbf{q} | \mathbf{l} \mathbf{k}) \hat{q} [f_0(E_{l' \mathbf{k} + \mathbf{q}}) - f_0(E_{l \mathbf{k}})]}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}}, \quad (1.24)$$

$$\mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_T = \frac{4\pi e^2}{\omega q m V} \sum_{l' \mathbf{k}} \frac{\hat{q} (\mathbf{l} \mathbf{k} | l' \mathbf{k} + \mathbf{q}) (l' \mathbf{k} + \mathbf{q} | \mathbf{p}_e + \hbar \mathbf{k} | \mathbf{l} \mathbf{k}) \cdot \mathbf{1}_T [f_0(E_{l' \mathbf{k} + \mathbf{q}}) - f_0(E_{l \mathbf{k}})]}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}}.$$

When the limit  $\mathbf{q} \rightarrow 0$  is taken, the dielectric constant tensor becomes

$$\boldsymbol{\epsilon}(0, \omega) = 1 - \frac{4\pi e^2 N}{m V \omega^2} + \frac{4\pi e^2}{m^2 V \omega^2} \sum_{l' \mathbf{k}} \frac{(\mathbf{l} \mathbf{k} | \mathbf{p}_e | l' \mathbf{k}) (l' \mathbf{k} | \mathbf{p}_e | \mathbf{l} \mathbf{k}) [f_0(E_{l' \mathbf{k}}) - f_0(E_{l \mathbf{k}})]}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k}}}. \quad (1.25)$$

In a crystal of cubic symmetry, the sum over the star of  $\mathbf{k}$ ,  $\sum_{\mathbf{k}^*} (\mathbf{l} \mathbf{k} | \mathbf{p}_e | l' \mathbf{k}) (l' \mathbf{k} | \mathbf{p}_e | \mathbf{l} \mathbf{k})$ , is a multiple of the unit dyadic, and consequently  $\boldsymbol{\epsilon}(0, \omega)$  is isotropic. Thus, with the approximations made to get Eq. (1.19), as  $\mathbf{q} \rightarrow 0$  the longitudinal and transverse dielectric constants become equal and  $\mathbf{1}_T \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_L$  and  $\mathbf{1}_L \cdot \boldsymbol{\epsilon}(\mathbf{q}, \omega) \cdot \mathbf{1}_T$  vanish. This is true for an arbitrary direction

of propagation in a cubic material, but will not in general hold in the case of crystals of lower symmetry.

## II. LOCAL-FIELD CORRECTIONS

In this section we will develop the theory of the longitudinal dielectric constant with local-field corrections, for a cubic insulating solid, in the case of wave-

lengths large relative to the lattice constant but small relative to the over-all crystal dimensions. Local-field effects arise in a real solid because the microscopic electric field varies rapidly over the unit cell. Consequently, the macroscopic field, which is the average of the microscopic field over a region large compared with the lattice constant but small compared with the wavelength  $2\pi/q$ , is not in general the same as the effective or local field which polarizes the charge in the crystal. For example, suppose a slowly varying external potential

$$\phi^{\text{ext}} = \phi^{\text{ext}}(\mathbf{q}, \omega) \exp i(\mathbf{q} \cdot \mathbf{r} - \omega t) \quad (2.1)$$

is applied to the crystal. The total potential  $\phi = \phi^{\text{ext}} + \phi^{\text{ind}}$  will in general contain rapidly varying terms with wave vector  $\mathbf{q} + \mathbf{K}$ , where  $\mathbf{K}$  is a vector of the reciprocal lattice:

$$\phi = \sum_{\mathbf{K}} \phi(\mathbf{q}, \mathbf{K}, \omega) \exp i[(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r} - \omega t]. \quad (2.2)$$

The potential  $\phi$  is the microscopic potential and determines how the charge in the crystal is polarized. The macroscopic potential  $\langle \phi \rangle_{\text{av}}$  is clearly given by

$$\langle \phi \rangle_{\text{av}} = \phi(\mathbf{q}, 0, \omega) \exp i(\mathbf{q} \cdot \mathbf{r} - \omega t), \quad (2.3)$$

since  $\exp(i\mathbf{q} \cdot \mathbf{r})$  is nearly constant over the averaging region while  $\exp[i(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r}]$ , ( $\mathbf{K} \neq 0$ ), is very rapidly

varying. The derivation in Sec. I assumed a potential of form Eq. (2.1) instead of Eq. (2.2). In other words, the distinction between the microscopic and macroscopic fields and potentials was neglected, with the result that no local-field corrections were obtained. In order to obtain the longitudinal dielectric constant with local-field corrections, a total potential of the form Eq. (2.2) must be assumed (with  $\mathbf{A} = 0$ ), and the induced potential,

$$\phi^{\text{ind}} = \sum_{\mathbf{K}} \phi^{\text{ind}}(\mathbf{q}, \mathbf{K}, \omega) \exp i[(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r} - \omega t], \quad (2.4)$$

must be calculated. The longitudinal dielectric constant is obtained from the *macroscopic* total and induced potentials<sup>4</sup> according to an alternative form of Eq. (1.2),

$$\hat{q} \cdot \epsilon^L(\mathbf{q}, \omega) \cdot \hat{q} = 1 - \langle \phi^{\text{ind}} \rangle_{\text{av}}(\mathbf{q}, \omega) / \langle \phi \rangle_{\text{av}}(\mathbf{q}, \omega). \quad (2.5)$$

Using Eq. (2.3), this is

$$\hat{q} \cdot \epsilon^L(\mathbf{q}, \omega) \cdot \hat{q} = 1 - \phi^{\text{ind}}(\mathbf{q}, 0, \omega) / \phi(\mathbf{q}, 0, \omega). \quad (2.6)$$

The right-hand side of Eq. (2.6) is easily evaluated in a formal manner. A calculation analogous to that of Sec. I gives the relation between  $\phi^{\text{ind}}$  and  $\phi$  as

$$\phi^{\text{ind}}(\mathbf{q}, \mathbf{K}, \omega) = |\mathbf{q} + \mathbf{K}|^{-2} \sum_{\mathbf{K}'} G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) \times \phi(\mathbf{q}, \mathbf{K}', \omega), \quad (2.7)$$

with

$$G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) = \frac{4\pi e^2}{V} \sum_{l' \mathbf{k}} \frac{(l\mathbf{k} | \exp(-i\mathbf{K} \cdot \mathbf{r}_e) | l'\mathbf{k} + \mathbf{q})(l'\mathbf{k} + \mathbf{q} | \exp(i\mathbf{K}' \cdot \mathbf{r}_e) | l\mathbf{k}) [f_0(E_{l\mathbf{k}}) - f_0(E_{l'\mathbf{k} + \mathbf{q}})]}{\hbar\omega + E_{l\mathbf{k}} - E_{l'\mathbf{k} + \mathbf{q}}}. \quad (2.8)$$

As before, the variable of integration in the matrix element has been indicated by  $\mathbf{r}_e$ . Let us define  $\epsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega)$  and  $\epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega)$  by

$$\epsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) = \delta_{\mathbf{K}, \mathbf{K}'} - G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) |\mathbf{q} + \mathbf{K}|^{-2}, \quad (2.9)$$

$$\sum_{\mathbf{K}''} \epsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'', \omega) \times \epsilon^{-1}(\mathbf{q} + \mathbf{K}'', \mathbf{q} + \mathbf{K}', \omega) = \delta_{\mathbf{K}, \mathbf{K}'}. \quad (2.10)$$

[The quantity  $\epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega)$  is just the dielectric response function of Schwinger and Martin.<sup>5</sup> Equations (2.9) and (2.10) have been given by Falk,<sup>6</sup> who treats the nearly free electron case.]

Rewrite Eq. (2.7) as

$$|\mathbf{q} + \mathbf{K}|^2 [\phi(\mathbf{q}, \mathbf{K}, \omega) - \phi^{\text{ind}}(\mathbf{q}, \mathbf{K}, \omega)] = \sum_{\mathbf{K}'} \epsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) |\mathbf{q} + \mathbf{K}'|^2 \phi(\mathbf{q}, \mathbf{K}', \omega), \quad (2.11)$$

and note that  $\phi(\mathbf{q}, \mathbf{K}, \omega) - \phi^{\text{ind}}(\mathbf{q}, \mathbf{K}, \omega) = \phi^{\text{ext}}(\mathbf{q}, \mathbf{K}, \omega) = \phi^{\text{ext}}(\mathbf{q}, \omega) \delta_{\mathbf{K}, 0}$ , since the external potential (the potential due to charges located outside the crystal) is essentially constant over a unit cell of the crystal. Using Eq. (2.10) we find

$$\phi(\mathbf{q}, \mathbf{K}, \omega) = |\mathbf{q} + \mathbf{K}|^{-2} \epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q}, \omega) q^2 \phi^{\text{ext}}(\mathbf{q}, \omega), \quad (2.12)$$

<sup>4</sup> L. Rosenfeld, *Theory of Electrons* (North-Holland Publishing Company, Amsterdam, 1951), Chap. 2.

<sup>5</sup> P. C. Martin and J. Schwinger, *Phys. Rev.* **115**, 1342 (1959).

<sup>6</sup> D. S. Falk, *Phys. Rev.* **118**, 105 (1960).

giving<sup>7</sup>

$$\hat{q} \cdot \epsilon(\mathbf{q}, \omega) \cdot \hat{q} = 1 / \epsilon^{-1}(\mathbf{q}, \mathbf{q}, \omega). \quad (2.13)$$

Thus, the problem of finding the dielectric constant with local field corrections reduces to that of solving the integral equation

$$\epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) = \delta_{\mathbf{K}, \mathbf{K}'} + \sum_{\mathbf{K}''} G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'', \omega) |\mathbf{q} + \mathbf{K}''|^{-2} \times \epsilon^{-1}(\mathbf{q} + \mathbf{K}'', \mathbf{q} + \mathbf{K}', \omega), \quad (2.14)$$

obtained by combining Eqs. (2.9) and (2.10).

The main purpose of this section is to develop a systematic method of approximating the integral equation (2.14). This will be accomplished by means of two successive transformations. First, the integral equation will be transformed from the  $\mathbf{K}$  representation to an  $\mathbf{r}$  representation, where  $\mathbf{r}$  is a continuous variable confined to a unit cell of the real lattice centered about the origin. In this representation, the kernel of the integral equation will be split into two parts,  $K^L$  and  $K^S$ . These describe the influence on a given cell of the field of the polarized charge in all other cells ( $K^L$ ) and of the field of the polarized charge in the same cell ( $K^S$ ), and are connected, respectively, with the local field and self-polarization corrections. A second transformation will

<sup>7</sup> This equation has been independently obtained by N. Wisser. I am indebted to M. H. Cohen and N. Wisser for communicating their results prior to publication.

then be made by expanding  $K^L$  in a multipole series, leading to an integral equation in what might be termed a multipole representation. This equation can be solved approximately by neglecting all but the first  $P$  multipole moments. The case when only dipole moments are retained will be worked out explicitly, and leads to a Lorenz-Lorentz formula modified by self-polarization corrections.

In the equations that follow, the  $\omega$  dependence of  $\epsilon^{-1}$  and  $G$  will no longer be indicated explicitly. To transform to the  $\mathbf{r}$  representation let us define

$$\epsilon^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}') = \sum_{\mathbf{K}, \mathbf{K}'} e^{i\mathbf{K} \cdot \mathbf{r}} e^{-i\mathbf{K}' \cdot \mathbf{r}'} \epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'), \quad (2.15)$$

$$G(\mathbf{q}, \mathbf{r}, \mathbf{r}') = \sum_{\mathbf{K}, \mathbf{K}'} e^{i\mathbf{K} \cdot \mathbf{r}} e^{-i\mathbf{K}' \cdot \mathbf{r}'} G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'). \quad (2.16)$$

The integral equation becomes

$$\begin{aligned} \epsilon^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}') &= v_a \sum_j \delta(\mathbf{r} - \mathbf{r}' - \mathbf{R}_j) + \frac{1}{v_a^2} \int_0^{v_a} d\mathbf{r}_1 d\mathbf{r}_1' \\ &\times G(\mathbf{q}, \mathbf{r}, \mathbf{r}_1) \left[ \frac{v_a}{4\pi} \sum_j \frac{\exp i\mathbf{q} \cdot (\mathbf{R}_j + \mathbf{r}_1' - \mathbf{r}_1)}{|\mathbf{R}_j + \mathbf{r}_1' - \mathbf{r}_1|} \right] \\ &\times \epsilon^{-1}(\mathbf{q}, \mathbf{r}_1', \mathbf{r}'), \quad (2.17) \end{aligned}$$

$$J[\mathbf{q}, f, g] = \frac{4\pi e^2}{V} \sum_{\substack{l, l' \\ (l \neq l')}} \frac{(l\mathbf{k} | f | l'\mathbf{k} + \mathbf{q}) (l'\mathbf{k} + \mathbf{q} | g | l\mathbf{k}) [f_0(E_{l\mathbf{k}}) - f_0(E_{l'\mathbf{k} + \mathbf{q}})]}{\hbar\omega + E_{l\mathbf{k}} - E_{l'\mathbf{k} + \mathbf{q}}}. \quad (2.21)$$

(No terms with  $l=l'$  appear in the summation in the case of an insulator because all bands are either empty or full.) The kernels  $G(\mathbf{q}, \mathbf{r}, \mathbf{r}_1')$ ,  $K^L(\mathbf{q}, \mathbf{r}, \mathbf{r}_1')$ , and  $K^S(\mathbf{q}, \mathbf{r}, \mathbf{r}_1')$  are obtained from this form by the substitutions

$$\begin{aligned} G, K^L, K^S: & f = V_a \sum_j \delta(\mathbf{r} - \mathbf{r}_e - \mathbf{R}_j), \\ G: & g = v_a \sum_j \delta(\mathbf{r}_1' - \mathbf{r}_e - \mathbf{R}_j), \\ K^L: & g = (v_a/4\pi) \exp[i\mathbf{q} \cdot (\mathbf{r}_1' - \mathbf{r}_e)] \\ & \times \sum_{j'} \exp(i\mathbf{q} \cdot \mathbf{R}_j) / |\mathbf{r}_e - \mathbf{r}_1' - \mathbf{R}_j|, \quad (2.22) \\ K^S: & g = (v_a/4\pi) \exp[i\mathbf{q} \cdot (\mathbf{r}_1' - \mathbf{r}_e)] / |\mathbf{r}_e - \mathbf{r}_1'|. \end{aligned}$$

The prime on the sum defining  $g$  in  $K^L$  means that the term with  $\mathbf{R}_j=0$  is to be omitted.

Since  $\mathbf{r}_1'$  and  $\mathbf{r}_e$  are restricted to lie within a unit cell

$$\mathbf{B}_p^L = \lim_{q \rightarrow 0} \left[ \frac{q}{v_a^2} \int_0^{v_a} d\mathbf{r}' d\mathbf{r}_1' \exp(i\mathbf{q} \cdot \mathbf{r}_1') T_p(\mathbf{q}, \mathbf{r}_1') \epsilon^{-1}(\mathbf{q}, \mathbf{r}_1', \mathbf{r}') \right], \quad (2.25)$$

and  $\mathbf{B}_1^S$  is the  $p=1$  case of

$$\mathbf{B}_p^S = \lim_{q \rightarrow 0} \left[ \frac{-iq}{v_a^2} \int_0^{v_a} d\mathbf{r}' d\mathbf{r}_1' \mathbf{K}_p^S(\mathbf{r}_1') \epsilon^{-1}(\mathbf{q}, \mathbf{r}_1', \mathbf{r}') \right]. \quad (2.26)$$

The kernels  $\mathbf{K}_{1p}^L$  and  $\mathbf{K}_p^S(\mathbf{r}_1')$  are obtained from Eq.

where  $\mathbf{R}_j$  are the vectors of the real lattice and the continuous variable  $\mathbf{r}$  is confined to a unit cell centered at  $\mathbf{R}_j=0$ . The inverse of the dielectric constant is obtained from

$$\epsilon^{-1}(\mathbf{q}, \mathbf{q}) = \frac{1}{v_a^2} \int_0^{v_a} d\mathbf{r} d\mathbf{r}' \epsilon^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}'). \quad (2.18)$$

The kernel of the integral equation,

$$\begin{aligned} K(\mathbf{q}, \mathbf{r}, \mathbf{r}_1') &= \frac{1}{v_a} \int_0^{v_a} d\mathbf{r}_1 G(\mathbf{q}, \mathbf{r}, \mathbf{r}_1) \frac{v_a}{4\pi} \\ &\times \sum_j \frac{\exp i\mathbf{q} \cdot (\mathbf{R}_j + \mathbf{r}_1' - \mathbf{r}_1)}{|\mathbf{R}_j + \mathbf{r}_1' - \mathbf{r}_1|}, \quad (2.19) \end{aligned}$$

can be divided into two parts,

$$K(\mathbf{q}, \mathbf{r}, \mathbf{r}_1') = K^L(\mathbf{q}, \mathbf{r}, \mathbf{r}_1') + K^S(\mathbf{q}, \mathbf{r}, \mathbf{r}_1'). \quad (2.20)$$

Since several kernels similar in structure will be introduced in the course of the derivation, we specify them all through the functional form

centered about the origin,  $|\mathbf{r}_e|/|\mathbf{r}_1' - \mathbf{R}_j| < 1$  for all  $\mathbf{R}_j \neq 0$  and the multipole expansion

$$\frac{v_a}{4\pi} \sum_j' \frac{\exp i\mathbf{q} \cdot \mathbf{R}_j}{|\mathbf{r}_e - \mathbf{r}_1' - \mathbf{R}_j|} = \sum_{p=0}^{\infty} (\mathbf{r}_e)^p \cdot \mathbf{T}_p(\mathbf{q}, \mathbf{r}_1') \quad (2.23)$$

is valid. Equation (2.23) serves as definition of the expansion coefficient  $\mathbf{T}_p$ . Substituting Eq. (2.17) into Eq. (2.18), splitting the kernel according to Eq. (2.20), making the multipole expansion of Eq. (2.23) and letting  $\mathbf{q} \rightarrow 0$  results in

$$\epsilon^{-1}(0, 0) = 1 - i \sum_{p=1}^{\infty} \hat{q} \cdot \mathbf{K}_{1p}^L \cdot \mathbf{B}_p^L + \mathbf{B}_1^S \cdot \hat{q}. \quad (2.24)$$

The quantity  $\mathbf{B}_p^L$  is defined by

(2.21) by substituting

$$\begin{aligned} K_{1p}^L: & f = \mathbf{r}_e, g = (\mathbf{r}_e)^p \\ K_p^S(\mathbf{r}_1'): & f = (\mathbf{r}_e)^p \exp(i\mathbf{q} \cdot \mathbf{r}_e), \\ & g = (v_a/4\pi) \exp[i\mathbf{q} \cdot (\mathbf{r}_1' - \mathbf{r}_e)] / |\mathbf{r}_1' - \mathbf{r}_e|. \quad (2.27) \end{aligned}$$

In deriving Eq. (2.24), the relation

$$\mathbf{q} \cdot (\mathbf{l}'\mathbf{k} + \mathbf{q} | \mathbf{r}_e \exp(i\mathbf{q} \cdot \mathbf{r}_e) | \mathbf{l}\mathbf{k}) = -i(\mathbf{l}'\mathbf{k} + \mathbf{q} | \mathbf{l}\mathbf{k}) + O(q^2), \quad (2.28)$$

valid when  $l \neq l'$ , has been used.

The kernels  $\mathbf{K}_{1,p}^L$  and  $\mathbf{K}_p^S(\mathbf{r}_1')$  are known quantities. In order to complete the set of equations, expressions for  $\mathbf{B}_p^L$  and  $\mathbf{B}_p^S$  must be derived. Multiplying Eq. (2.17) by  $q \exp(i\mathbf{q} \cdot \mathbf{r}_1') \mathbf{T}_p(\mathbf{q}, \mathbf{r}_1')$  and integrating gives

$$\mathbf{B}_p^L = i\hat{q}\delta_{p,1} + \sum_{k=1}^{\infty} (-1)^k \binom{k+p}{k} \left[ \lim_{q \rightarrow 0} \mathbf{T}_{k+p}(\mathbf{q}, 0) \right] \cdot (i\mathbf{B}_k^S + \sum_{n=1}^{\infty} \mathbf{K}_{kn}^L \cdot \mathbf{B}_n^L), \quad (2.29)$$

where the kernel  $\mathbf{K}_{kn}^L$  is obtained from Eq. (2.21), by the substitution

$$\mathbf{K}_{kn}^L: f = (\mathbf{r}_e)^k, \quad g = (\mathbf{r}_e)^n. \quad (2.30)$$

In the first term on the right-hand side of Eq. (2.29) the evaluation

$$\lim_{q \rightarrow 0} \frac{q}{v_a} \int_0 d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \mathbf{T}_p(\mathbf{q}, \mathbf{r}) = i\hat{q}, \quad p=1, \\ = 0, \quad p > 1, \quad (2.31)$$

has been used.<sup>8</sup> Finally, an equation for the  $\mathbf{B}_p^S$  must be derived. Let us write

$$D(\mathbf{q}, \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - (1/v_a) K^S(\mathbf{q}, \mathbf{r}, \mathbf{r}'), \quad (2.32)$$

and define  $D^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}_1)$  by

$$(1/v_a) \int_0 d\mathbf{r}_1 D^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}_1) D(\mathbf{q}, \mathbf{r}_1, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (2.33)$$

Then we can write

$$\epsilon^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}') = D^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}') + (1/v_a^2) \int_0 d\mathbf{r}_1 d\mathbf{r}_1' D^{-1}(\mathbf{q}, \mathbf{r}, \mathbf{r}_1) \times K^L(\mathbf{q}, \mathbf{r}_1, \mathbf{r}_1') \epsilon^{-1}(\mathbf{q}, \mathbf{r}_1', \mathbf{r}'). \quad (2.34)$$

Multiplying Eq. (2.34) by  $-i\hat{q} \mathbf{K}_p^S(\mathbf{r})/v_a^2$ , integrating and making a multipole expansion gives

$$\mathbf{B}_p^S = \frac{-i}{v_a^2} \sum_{n=1}^{\infty} \int_0 d\mathbf{r} d\mathbf{r}_1 \times \mathbf{K}_p^S(\mathbf{r}) D^{-1}(0, \mathbf{r}, \mathbf{r}_1) \mathbf{K}_n^L(\mathbf{r}_1) \cdot \mathbf{B}_n^L, \quad (2.35)$$

where  $\mathbf{K}_n^L(\mathbf{r}_1)$  is defined by

$$\mathbf{K}_n^L(\mathbf{r}_1): f = v_a \sum_j \delta(\mathbf{r}_1 - \mathbf{r}_e - \mathbf{R}_j), \quad g = (\mathbf{r}_e)^n. \quad (2.36)$$

<sup>8</sup> This is easily obtained by using

$$\frac{v_a}{4\pi} \sum_j \frac{\exp(i\mathbf{q} \cdot \mathbf{R}_j)}{|\mathbf{r}_e - \mathbf{r} - \mathbf{R}_j|} = \sum_{\mathbf{K}} \frac{\exp[i(\mathbf{q} + \mathbf{K}) \cdot (\mathbf{r}_e - \mathbf{r})]}{|\mathbf{q} + \mathbf{K}|^2}.$$

It should be noted that terms involving  $\mathbf{B}_0^L$  have been omitted from Eqs. (2.24), (2.29) and (2.35) because they vanish in the limit  $\mathbf{q} \rightarrow 0$ . For example, the coefficient of  $\mathbf{B}_0^L$  in Eq. (2.24) contains a factor  $(\mathbf{l}'\mathbf{k} + \mathbf{q} | \exp(-i\mathbf{q} \cdot \mathbf{r}_e) | \mathbf{l}\mathbf{k})$ . Since

$$(\mathbf{l}'\mathbf{k} + \mathbf{q} | \exp(-i\mathbf{q} \cdot \mathbf{r}_e) | \mathbf{l}\mathbf{k}) = (\mathbf{l}'\mathbf{k} + \mathbf{q} | \mathbf{l}\mathbf{k}) - i\mathbf{q} \cdot (\mathbf{l}'\mathbf{k} + \mathbf{q} | \mathbf{r}_e | \mathbf{l}\mathbf{k}) + O(q^2) = O(q^2)$$

and

$$\mathbf{B}_0^L = \frac{q}{v_a} \int_0 d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{v_a}{4\pi} \sum_j' \frac{\exp(i\mathbf{q} \cdot \mathbf{R}_j)}{|\mathbf{r} + \mathbf{R}_j|} \sim \frac{q}{v_a} \int_0 d\mathbf{r} \sum_{\mathbf{K}} \frac{\exp(i\mathbf{K} \cdot \mathbf{r})}{|\mathbf{K} + \mathbf{q}|^2} = \frac{1}{q}$$

the term drops out as  $\mathbf{q} \rightarrow 0$ . Similarly, the terms in Eq. (2.29) and Eq. (2.35) involving  $\mathbf{B}_0^L$  do not contribute.

The preceding manipulations have replaced the integral equation (2.14) for  $\epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}')$  by Eqs. (2.29) and (2.35), which together constitute an integral equation for  $\mathbf{B}_p^L$  ( $p=1, \dots, \infty$ ), and the integral Eq. (2.33) for  $D^{-1}$ . Once the quantities  $\mathbf{B}_p^L$  and  $\mathbf{B}_1^S$  are known, the dielectric constant with local-field corrections can be calculated from Eq. (2.24). The point of this formal rearrangement is that it is now possible to make an approximation with a clear physical significance which makes Eqs. (2.29) and (2.35) easily soluble. This is simply to neglect all the  $\mathbf{B}_p^L$  with  $p$  greater than some integer  $P$ . This means roughly that we are approximating the influence on a given cell of the charge in any other cell by the first  $P$  multipole moments of this charge. In many cases, we expect very good results to be obtained for a small value of  $P$ . The most familiar case is that of  $P=1$  (dipole approximation). Utilizing the fact that the only second-order tensor compatible with cubic symmetry is the isotropic tensor, and noting that the inhomogeneous term in the equation for  $\mathbf{B}_1^L$  is a vector parallel to  $\mathbf{q}$ , Eqs. (2.24), (2.29), and (2.35) become

$$\epsilon^{-1}(0,0) = 1 - i\mathbf{B}_1^L \cdot \hat{q} \hat{q} \cdot \mathbf{K}_{11}^L \cdot \hat{q} + \mathbf{B}_1^S \cdot \hat{q}, \\ \mathbf{B}_1^L \cdot \hat{q} = i - 2 \left[ \lim_{q \rightarrow 0} \hat{q} \cdot \mathbf{T}_2(\mathbf{q}, 0) \cdot \hat{q} \right] \times (i\mathbf{B}_1^S \cdot \hat{q} + \hat{q} \cdot \mathbf{K}_{11}^L \cdot \hat{q} \mathbf{B}_1^L \cdot \hat{q}), \\ \mathbf{B}_1^S \cdot \hat{q} = -(i/v_a^2) \hat{q} \cdot \int_0 d\mathbf{r} d\mathbf{r}_1 \times \mathbf{K}_1^S(\mathbf{r}) D^{-1}(0, \mathbf{r}, \mathbf{r}_1) K_1^L(\mathbf{r}_1) \cdot \hat{q} \mathbf{B}_1^L \cdot \hat{q} \\ \equiv -i4\pi C_1 \mathbf{B}_1^L \cdot \hat{q}. \quad (2.37)$$

It is easy to show that

$$\hat{q} \cdot \mathbf{K}_{11}^L \cdot \hat{q} = -4\pi\alpha, \quad (2.38)$$

where  $\alpha$  is the polarizability calculated without making local-field corrections. [The second term on the right of Eq. (1.21) is just  $4\pi\alpha$ .] The dipole sum  $\hat{q} \cdot \mathbf{T}_2(\mathbf{q}, 0) \cdot \hat{q}$  is not absolutely convergent. However, if we evaluate it in a crystal of finite diameter  $L$ , letting  $L \rightarrow \infty$  and  $q \rightarrow 0$  while keeping  $qL \gg 1$ , it has the value  $-\frac{1}{3}$ , independent of the crystal shape.<sup>9</sup> This evaluation procedure is the one that makes sense physically for wavelengths in the infrared, visible and near ultraviolet. For such wavelengths and for a typical crystal of dimension  $L$  and lattice constant  $a$ , the inequality  $qL \gg 1$  holds. However, since  $qa \ll 1$  and since the matrix elements and energies appearing in the kernels vary appreciably only when  $q$  changes by an amount of order  $1/a$ , we can still take the limit  $\mathbf{q} \rightarrow 0$  in the kernels.

Using these evaluations, Eqs. (2.37) may be readily solved to yield

$$\frac{1}{\epsilon^{-1}(0,0)} = 1 + \frac{4\pi(\alpha - C_1)}{1 - (4\pi/3)(\alpha - C_1)}. \quad (2.39)$$

This is the usual Lorenz-Lorentz formula, modified by the subtraction from  $\alpha$  of

$$C_1 = (1/4\pi v_a^2) \hat{q} \cdot \int_0 \mathbf{r} d\mathbf{r} \mathbf{r}_1 \times \mathbf{K}_1^S(\mathbf{r}) \langle \mathbf{r} | [1 - (1/v_a)K^S]^{-1} | \mathbf{r}_1 \rangle \mathbf{K}_1^L(\mathbf{r}_1) \cdot \hat{q}. \quad (2.40)$$

This self-polarization correction takes just the form that is expected on the basis of a simple classical model. If we compute the dielectric constant of a macroscopic cubic lattice of uniform spheres composed of material of polarization per unit volume  $\alpha$ , we find that the dielectric constant is determined by a Lorenz-Lorentz formula, except that  $\alpha$  is replaced by

$$\alpha' = \alpha - \frac{4\pi\alpha^2/3}{1 + 4\pi\alpha/3}. \quad (2.41)$$

The subtracted term is a self-polarization correction arising from the influence on a given sphere of its surface charge. To examine the qualitative form of  $C_1$ , let us replace all the kernels  $K$  appearing in Eq. (2.40) by  $-4\pi\alpha$  [cf. Eq. (2.38)]. Then we see that the correction  $C_1$  also has the form  $A\alpha^2/(1+B\alpha)$ , with  $A, B > 0$ .

With the formalism developed, higher-order corrections to the Lorenz-Lorentz formula can be obtained by

taking the cutoff integer  $P$  larger than one. Note that  $\mathbf{T}_p(0,0)$  is absolutely convergent for  $p > 2$ , so no additional ambiguities regarding the method of summation appear when working to higher order. Although the calculation has been carried out for crystals of cubic symmetry in order to avoid a tensor dielectric constant, its main features would be expected to carry over to the case of arbitrary symmetry. If the restriction to insulators is dropped, intraband terms ( $l=l'$ ) appear in Eq. (2.21). If these are treated in a free-electron approximation, which should be reasonable when motion of the conduction electrons and holes is well described by an effective mass, the generalization of the above derivation is straightforward and leads to

$$\frac{1}{\epsilon^{-1}(0,0)} = 1 + 4\pi\alpha^I + \frac{4\pi(\alpha^{II} - C_1)}{1 - (4\pi/3)(\alpha^{II} - C_1)}. \quad (2.42)$$

In Eq. (2.42)  $\alpha^I$  and  $\alpha^{II}$  are, respectively, the intraband ( $l=l'$ ) and interband ( $l \neq l'$ ) parts of  $\alpha$ , the polarizability without local field corrections. The restriction  $qL \gg 1$ , necessary to evaluate the dipole wave sum  $\mathbf{T}_2(\mathbf{q}, 0)$ , cannot be relaxed without drastically altering the derivation. In order to deal with wavelengths comparable with the macroscopic dimensions of the crystal it would be necessary to take into account surface effects, which of course has not been done in the above derivation.

#### ACKNOWLEDGMENT

The author wishes to thank Dr. H. Ehrenreich for suggesting the problem treated in this paper and for many helpful discussions.

#### APPENDIX

In order to prove that the expression for  $\mathbf{j}^{\text{ind}}(\mathbf{q}, \omega)$  is gauge invariant, we need the auxiliary identities:

$$\sum_l u_{lk}(\mathbf{r}) u_{lk}^*(\mathbf{r}') = v_a \sum_j \delta(\mathbf{r} - \mathbf{r}' - \mathbf{R}_j), \quad (\text{A1})$$

$$\mathbf{q} \cdot (l\mathbf{k} | p_e + \hbar\mathbf{k} + \hbar\mathbf{q} / 2 | l'\mathbf{k} + \mathbf{q}) = (m/\hbar)(E_{l\nu_{\mathbf{k}+\mathbf{q}}} - E_{l\nu_{\mathbf{k}}}) (l\mathbf{k} | l'\mathbf{k} + \mathbf{q}). \quad (\text{A2})$$

Expression (A1) is just the completeness relation for the periodic parts of the Bloch functions. The identity (A2) is obtained in a straightforward manner by writing  $\mathbf{k} \cdot \mathbf{p}$  Schrödinger equations for  $u_{lk}^*$  and  $u_{l\nu_{\mathbf{k}+\mathbf{q}}}$ , multiplying the former by  $u_{l\nu_{\mathbf{k}+\mathbf{q}}}$ , the latter by  $u_{lk}^*$ , and subtracting. We may also regard (A2) as the result of expanding

$$\int d\mathbf{r} \exp(-i\mathbf{q} \cdot \mathbf{r}) [\nabla \cdot \langle l\mathbf{k} | \mathbf{j}_{\text{op}}^{(0)}(\mathbf{r}) | l'\mathbf{k} + \mathbf{q} \rangle + \partial \langle l\mathbf{k} | \rho_{\text{op}}^{(0)}(\mathbf{r}) | l'\mathbf{k} + \mathbf{q} \rangle / \partial t] = 0, \quad (\text{A3})$$

which shows that it is an expression of conservation of charge in the unperturbed theory.

<sup>9</sup> M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

Let us now make the gauge transformation  $\mathbf{A} \rightarrow \mathbf{A} + \mathbf{q}f(\mathbf{q}, \omega)$ ,  $\phi \rightarrow \phi + (\omega/c)f(\mathbf{q}, \omega)$ . Then

$$\begin{aligned} \Delta \mathbf{j}^{\text{ind}}/f(\mathbf{q}, \omega) &= -e^2 N \mathbf{q}/mcV \\ &- \frac{e^2}{m^2 c V} \sum_{l' \mathbf{k}} \frac{(l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l' \mathbf{k} + \mathbf{q}) [f_0(E_{l \mathbf{k}}) - f_0(E_{l' \mathbf{k} + \mathbf{q}})] (l' \mathbf{k} + \mathbf{q} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l \mathbf{k}) \cdot \mathbf{q}}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}} \\ &+ \frac{e^2 \omega}{mcV} \sum_{l' \mathbf{k}} \frac{(l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l' \mathbf{k} + \mathbf{q}) [f_0(E_{l \mathbf{k}}) - f_0(E_{l' \mathbf{k} + \mathbf{q}})]}{\hbar \omega + E_{l \mathbf{k}} - E_{l' \mathbf{k} + \mathbf{q}}}. \end{aligned}$$

Combining terms gives

$$\begin{aligned} \Delta \mathbf{j}^{\text{ind}}/f(\mathbf{q}, \omega) &= (e^2/mcV) \{ -N \hbar \mathbf{q} + \sum_{l' \mathbf{k}} (l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l' \mathbf{k} + \mathbf{q}) [f_0(E_{l \mathbf{k}}) - f_0(E_{l' \mathbf{k} + \mathbf{q}})] (l' \mathbf{k} + \mathbf{q} | l \mathbf{k}) \} \\ &= (e^2/mcV) [ -N \hbar \mathbf{q} + 2 \sum_{l \mathbf{k}} f_0(E_{l \mathbf{k}}) \sum_{l' \mathbf{k}} (l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l' \mathbf{k} + \mathbf{q}) (l' \mathbf{k} + \mathbf{q} | l \mathbf{k}) \\ &= (e^2/mcV) [ -N \hbar \mathbf{q} + 2 \sum_{l \mathbf{k}} f_0(E_{l \mathbf{k}}) (l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} + \hbar \mathbf{q}/2 | l \mathbf{k}) ] = 0. \quad (\text{A4}) \end{aligned}$$

In the last step, the fact that  $(l \mathbf{k} | \mathbf{p}_e + \hbar \mathbf{k} | l \mathbf{k})$  has odd parity under inversion of  $\mathbf{k}$  has been used.